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Separation of Uranium and Protactinium from Thorium by Amine Extraction

By Fujio ICHIKAWA and Shinobu URUNO

(Received September 18, 1959)

Preuss and Saunders[1] reported the extraction of uranium from sulfuric acid solution with amines. The use of primary amine as an extractant for thorium from sulfuric acid was reported by Crous and Denis[2]. Moore and his coworkers studied the liquid-liquid extraction of protactinium, niobium, tantalum, cobalt and zinc by amine[3-5].

In this paper, the extraction of thorium, protactinium and uranium from hydrochloric, nitric and sulfuric acid of various concentrations with secondary amine is studied. Amberlite LA-1 in kerosene diluent is used as an extractant.

The free-base form of Amberlite LA-1 removes acids from aqueous solutions by neutralization as illustrated by reaction 1,

$$(RR'NH)_{org} + H^+ + A^- \rightleftarrows (RR'NH_2A)_{org} \quad (1)$$

where the ions, H^+ and A^-, refer to the aqueous phase and "org" refers to the amine salt dissolved in the organic solvent. When the amine salt formed through neutralization is brought into contact with an aqueous solution which contains another anion, the exchange of anions associated with the amine salt takes place as shown by reaction 2,

$$(RR'NH_2A)_{org} + B^- \rightleftarrows (RR'NH_2B)_{org} + A^- \quad (2)$$

where A^- and B^- represent two different anions.

When an element exists as a complex anion in an aqueous medium, it will be extracted by the amine according to this exchange process. Then it is of interest to compare the acid dependency of the extraction coefficient of an element by the amine with that of the distribution coefficient of the same element by the anion exchange resin. From the result of the extraction study, it is found that under the optimum conditions uranium, protactinium and thorium can be separated from each other. This separation procedure will be suitable for the recovery of uranium-233 from irradiated thorium blanket fuel. Consequently, the radiation damage of Amberlite LA-1 and LA-2 is studied by two methods.

The Extraction Coefficient of Thorium, Protactinium and Uranium from Hydrochloric, Nitric and Sulfuric Acid of Various Concentrations by Amberlite LA-1

Experimental.—Two milliliters each of 5% Amberlite LA-1 in a kerosene diluent is shaken in a small glass-stopped tube for 1 min. with the same volume of an acid solution of the sample. After centrifuging, 1 ml. each of the aqueous and the organic phases are pipetted out and the concentration of the element is measured as follows. Thorium-234 (UX_1) and protactinium-233 are used as tracers for thorium and protactinium, and the γ-ray activity is measured with a well-type scintillation counter. Uranium nitrate is used as the starting material

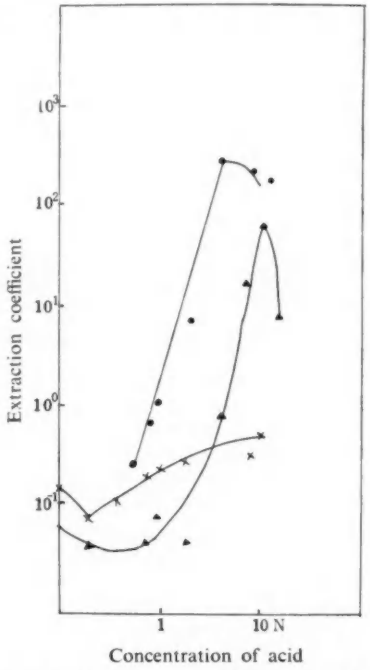

Fig. 1. Extraction coefficient of Th, Pa and U from HCl with Amberlite LA-1.
U —●—, Pa —▲—, Th —×—

1) A. Preuss and J. Saunders, RMO-2533 (1955).
2) D. J. Crous and J. O. Denis, ORNL-1859 (1955).
3) J. Y. Ellenburg, G. W. Leddicotte and F. L. Moore, *Anal. Chem.*, **26**, 1045 (1954).
4) H. A. Mahlman, G. W. Leddicotte and F. L. Moore, ibid., **26**, 1939 (1954).
5) F. L. Moore, ibid., **27**, 70 (1955).

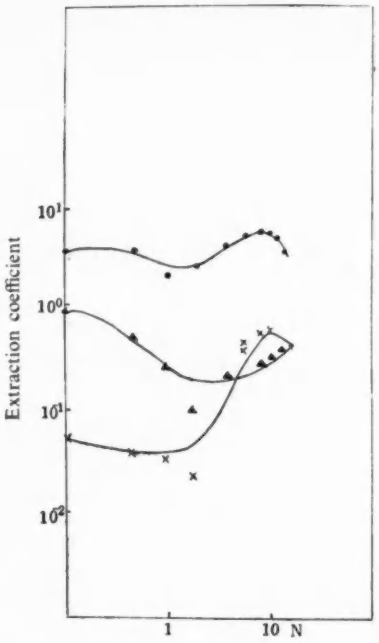

Fig. 2. Extraction coefficient of Th, Pa and U from HNO_3 with Amberlite LA-1.
U —●—, Pa —▲—, Th —×—

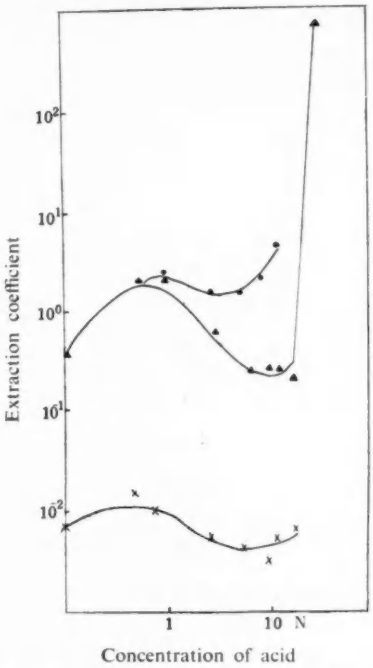

Fig. 3. Extraction coefficient of Th, Pa and U from H_2SO_4 with Amberlite LA-1.
U —●—, Pa —▲—, Th —×—

for extraction and its concentration is determined colorimetrically with hydrogen peroxide. The extraction coefficient is calculated by the following equation,

$$E = \frac{\text{Concentration of U, Th or Pa in organic phase/ml.}}{\text{Concentration of U, Th or Pa in aqueous phase/ml.}}$$

where E is the extraction coefficient. The results are shown in Figs. 1—3.

Results.—The maximum extraction coefficient of uranium is about 200 at 6~12 N hydrochloric acid and below this concentration the extraction coefficient decreases with a slope of 3. From nitric acid solution, uranium is extractable in all the concentration ranges examined, giving an extraction coefficient of 2~5. The extraction coefficient of 1~3 is also found from 1~12 N sulfuric acid solution. Thorium is not extracted from these acids except 6~15 N nitric acid, but the extraction coefficient is only 0.5 even under this condition. Protactinium is favorably extracted from hydrochloric acid of higher concentration with a maximum extraction coefficient of 60. From nitric or sulfuric acid the extraction coefficient of protactinium is very low.

Comparison of Extraction Coefficient with Distribution Coefficient

If the amine extraction is based on the anion exchange mechanism, it is valuable to compare the amine extraction curve with the acid dependency of the distribution coefficient of these elements by anion exchange resin. From this view-point, the distribution coefficient (Kd) of thorium, protactinium and uranium between hydrochloric, nitric and sulfuric acids of various concentrations and anion exchange resin are measured by the following method.

Experimental.—Dowex 1 ×8 (100~200 mesh) is used as an anion exchange resin. It is treated with 10% sodium hydroxide solution, washed with water and then converted into the desired form with hydrochloric, nitric or sulfuric acid. Half a gram of dried resin is placed for 24 hr. in 5 ml. of the acid solution of thorium, protactinium or uranium. The solution is filtered and the concentration of 1 ml. of filtrate is compared with that of the reference solution which contains no resin. Kd is calculated by the following equation,

$$Kd = \frac{\text{C(1 g. of resin)}}{\text{C(1 ml. of solution)}} = \frac{\text{C(reference)} - \text{C(filtrate)}}{\text{C(filtrate)}} \times 10$$

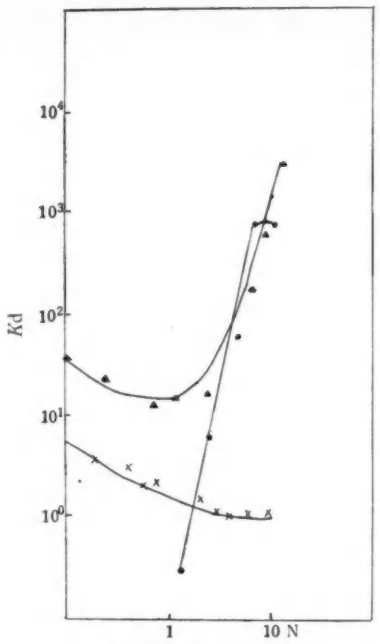

Fig. 4. Distribution coefficient of Th, Pa and U between Dowex 1 and HCl.
U —●—, Pa —▲—, Th —×—

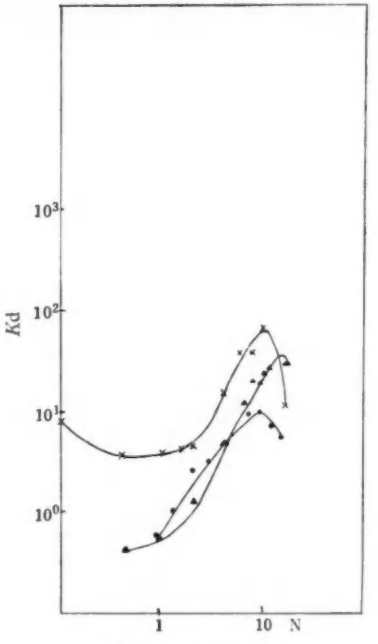

Fig. 5. Distribution coefficient of Th, Pa and U between Dowex 1 and HNO_3.
U —●—, Pa —▲—, Th —×—

where C means the concentration.

UX_1 and Pa-233 are used as tracers for thorium and protactinium, respectively. Their γ-ray activities are measured to determine the concentration. The concentration of uranium is determined by the colorimetric method.

Results.—The results are shown in Figs. 4—6. Concerning the anion exchange of these elements, some studies have already been reported by Kraus, Nelson and Danon[6,7]. In hydrochloric acid solution, the shapes of *K*d curves resemble those of extraction curves by LA-1, but the extraction coefficient of uranium is relatively very high. In a more concentrated nitric acid, Fig. 5 shows the order of adsorption as Th> Pa>U, but Fig. 2 shows the order of extraction as U>Th>Pa. In sulfuric acid, uranium is most favorably extractable with the amine, but Fig. 6 shows nearly the same *K*d value of uranium and protactinium.

These facts show that Amberlite LA-1 is selective in the extraction of uranium. It is not clear from these data whether or not this selectivity is due to the difference in the mechanism of amine extraction and anion exchange.

6) K. A. Kraus and F. Nelson, A/Conf. 8/P/837 (1955).
7) J. Danon, *J. Am. Chem. Soc.*, **78**, 5935 (1956).

The Separation of Uranium, Protactinium and Thorium by Amberlite LA-1

According to the study of the extraction coefficient, uranium and protactinium are sufficiently extracted from 8 N hydrochloric acid, but thorium is not extracted from hydrochloric acid of any concentration. At 3 N hydrochloric acid, the extraction coefficients are about 35, 0.1 and 0.05 for uranium, protactinium and thorium, respectively. From these facts, the separation of these elements is studied as follows.

Experimental.—*a) The separation of thorium and protactinium from 8N hydrochloric acid.*—Fifty milligrams of thorium nitrate is irradiated in the J. R. R.-1 Reactor for 2 hr. at a flux of 10^{11} neutrons/cm^2/sec. The irradiated sample is dissolved in 2 ml. of 8 N hydrochloric acid and extracted with 5% Amberlite LA-1 (HCl form) in kerosene. The organic phase is scrubbed three times with 3 ml. each of 8 N hydrochloric acid, then stripped three times with 2 ml. each of 0.1 N hydrochloric acid. γ-Ray activity of about 3.8×10^6 c. p. m. of protactinium is collected in the stripping solution and thorium is not detected by thorin in this solution. The recovery of protactinium is about 80%.

b) The effect of kerosene diluent on the extraction coefficient.—The effect of kerosene diluent is tested

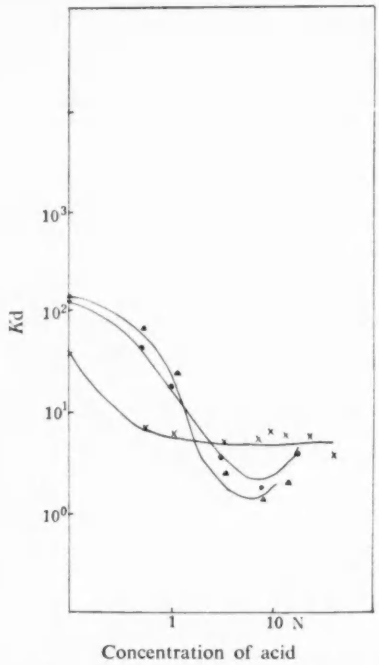

Fig. 6. Distribution coefficient of Th, Pa and U between Dowex 1 and H_2SO_4.
U —●—, Pa —▲—, Th —×—

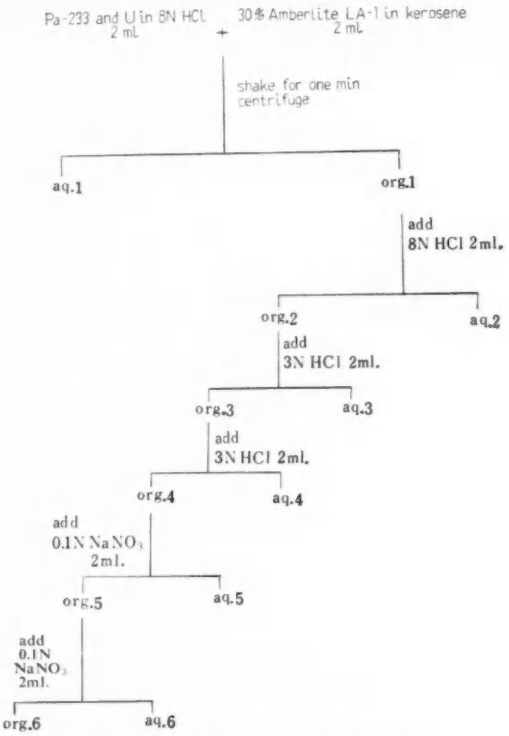

Fig. 7. Procedure of separating uranium and protactinium.

by calculating the extraction coefficient of protactinium from 8 N hydrochloric acid. From zero to 37.5% LA-1 in kerosene is used as an extractant. Two milliliters each of aqueous and organic phases are shaken for 1 min. and centrifuged. The extraction coefficient is determined as explained above. The results are shown in Table I. The effect of the diluent is negligible within the concentration of 2.5 to 37.5% LA-1 in kerosene.

Table I. The effect of diluent to the extraction coefficient of protactinium from 8 N HCl

The concentration of Amberlite LA-1 in kerosene	Extraction coefficient of Pa from 8 N HCl
0 %	0.05
0.5	27
2.5	194
5.0	150
7.5	158
12.5	256
17.0	143
37.5	197

c) *Stripping of uranium.*—About 10 mg. of uranium is extracted from 2 ml. of 8 N hydrochloric acid with 2 ml. of 30% Amberlite LA-1 in kerosene. Then, uranium is stripped from the organic phase with sodium nitrate, ammonium sulfate and sodium carbonate of various concentrations. The concentration of uranium in aqueous phase is measured colorimetrically with hydrogen peroxide. The results are shown in Table II.

Table II shows that uranium is completely stripped from the organic phase with 0.1 N sodium nitrate.

Table II. Recovery of uranium from 30% Amberlite LA-1 in kerosene

Concentration of stripping agent	Distilled water	$NaNO_3$	$(NH_4)_2SO_4$	Na_2CO_3
0 N	106%	—	—	—
〃	119	—	—	—
〃	120	—	—	—
0.1	—	100 %	88.4%	82.0%
〃	—	102	—	—
〃	—	105	—	—
0.5	—	94.0	89.4	75.0
1.0	—	89.8	54.3	94.0
2.0	—	80.5	60.5	—
4.0	—	54.6	—	—
5.0	—	30.5	54.3	87.6

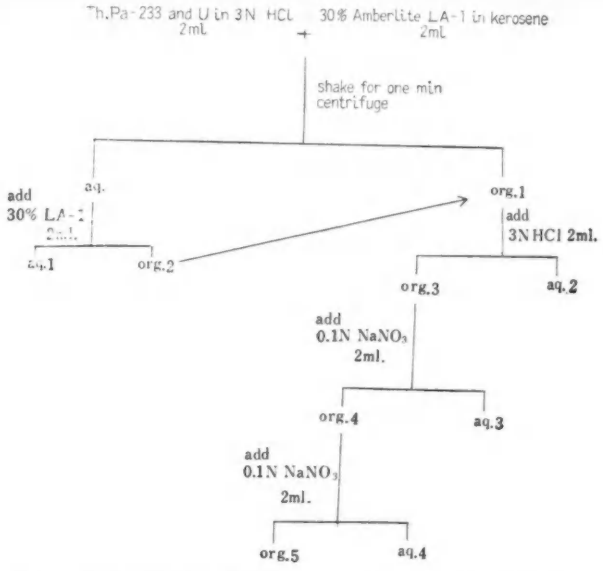

Fig. 8. Procedure of separating uranium from irradiated thorium.

Recovery with 0.1 N ammonium sulfate is 88.4%. The recovery of uranium decreases with the increase of the concentration of sodium nitrate or ammonium sulfate. Recovery with sodium carbonate is 75~94 %. When distilled water is used as a stripping agent, two phases do not separate even after centrifugation and colorimetric data show a higher value. Consequently, the best stripping agent is 0.1 N sodium nitrate.

d) The separation of protactinium and uranium by 3N hydrochloric acid scrubbing.—The separation scheme is shown in Fig. 7. Two milliliters of 8 N hydrochloric acid solution of protactinium-233 and uranium is shaken with 2 ml. of 30% Amberlite LA-1 in kerosene for 1 min. Most of the protactinium and uranium are extracted in this procedure. The organic phase is scrubbed with 2 ml. of 8 N hydrochloric acid, then protactinium is stripped twice with 3 N hydrochloric acid. Finally uranium is stripped twice with 0.1 N sodium nitrate. The results are shown in Table III. It is seen from these results that protactinium-233 is sufficiently extracted from 8 N hydrochloric acid and easily stripped with 3 N hydrochloric acid and that uranium is also sufficiently extracted from 8 N hydrochloric acid and about 40% of uranium is stripped with 3 N hydrochloric acid. Sixty per cent of the uranium is recovered with a slight contamination of protactinium-233 in this procedure. Thorium is not extracted under the condition explained above.

e) The extraction of uranium from thorium and protactinium in 3N hydrochloric acid solution.—About 50 mg. of thorium nitrate is irradiated in the J. R. R.-1 Reactor. After irradiation, 20 mg. of uranium is added to this sample and the mixture is dissolved in 2 ml. of 3 N hydrochloric acid. Two milliliters of Amberlite LA-1 in kerosene is added to this solution and the solution is shaken for 1 min. After centrifuging, the aqueous phase is re-extracted with 2 ml. of 30% LA-1 solution. Two organic phases are scrubbed with 2 ml. of 3 N hydrochloric acid. Uranium is stripped twice with 2 ml. each of 0.1 N sodium nitrate. The activity of protactinium-233 is measured by γ-ray counting. The Recovery of uranium is determined by the colorimetric method. Fig. 8 shows the separation scheme. Results are shown in Table IV.

TABLE III. RECOVERY* OF PROTACTINIUM AND URANIUM

Sample No.	Medium	Recovery of Pa-233	Recovery of U
aq. 1+aq. 2	8 N HCl	1.3%	8.4%
aq. 3+aq. 4	3 N HCl	98.0	35.7
aq. 5+aq. 6	0.1 N $NaNO_3$	0.3	70.0
org. 6	30% Amberlite LA-1 in kerosene	0.4	—

* This ratio is calculated by two experiments.

Table IV. RECOVERY* OF PROTACTINIUM AND URANIUM

Sample No.	Medium	Recovery of Pa-233	Recovery of U
aq. 1+aq. 2	3 N HCl	98.5%	0%
aq. 3+aq. 4	0.1 N $NaNO_3$	0.5	100
Org. 5	30% Amberlite LA-1 in kerosene	0.7	—

* This ratio is calculated by two experiments.

Table V. Radiation damage of Amberlite LA-1 and LA-2

Sample No.	Amine	Distance from Co-60	Dose rate	Irradiation time	Total dose	Exchange capacity	Extraction coefficient of Pa from 8 N HCl
		cm.	r/hr.	hr. min.	r	meq./ml.	
1	Amberlite LA-1	12.5	5.6×10^5	89 20	5×10^7	2.03	130
2	〃	〃	〃	17 50	1×10^7	2.03	125
3	〃	10	8.1×10^5	6 16	5×10^6	2.03	134
4	〃	〃	〃	1 15	1×10^6	2.03	124
5	〃	15	4.2×10^5	1 12	5×10^5	2.01	122
6	〃	30	1.3×10^5	48	1×10^5	2.01	152
7	〃	50	4.4×10^4	1 08	5×10^4	2.01	173
8	〃	—	0	0	0	2.03	183
9	Amberlite LA-2	12.5	5.6×10^5	89 20	5×10^7	2.03	83
10	〃	〃	〃	17 50	1×10^7	2.03	92
11	〃	10	8.1×10^5	6 16	5×10^6	2.03	110
12	〃	〃	〃	1 15	1×10^6	2.03	87
13	〃	15	4.2×10^5	1 12	5×10^5	2.01	86
14	〃	30	1.3×10^5	48	1×10^5	2.01	86
15	〃	50	4.4×10^4	1 08	5×10^4	2.03	87
16	〃	—	0	0	0	2.03	85

Uranium is completely recovered from the first solution by this procedure.

Radiation Damage of Amberlite LA-1 and LA-2

If these amines are used in reactor fuel reprocessing, radiation damage may occur on the action of high level γ-rays. Amberlite LA-1 and LA-2 are irradiated by γ-rays from Co-60 under various conditions (Table V). The degree of radiation damage is measured by extraction of protactinium-233 from 8 N hydrochloric acid and by potentiometric titration in dioxane. Two milliliters of irradiated sample is dissolved in 50 ml. of dioxane and is titrated with 0.2 N perchloric acid in dioxane. The end point is determined by drawing the potentiometric titration curve. A pH meter is used as a potentiometer. A calomel electrode, of which the aqueous solution of potassium chloride is displaced by saturated methanol solution of potassium chloride[8], is used as a reference electrode. A platinum electrode is used as an indicating electrode. The typical titration curve is shown in Fig. 9. The results are shown in Table V. Another method is to measure the extraction coefficient of protactinium-233 from 8 N hydrochloric acid by 30% irradiated amine in kerosene. The extraction coefficient is determined as mentioned above. Results are also shown in Table V. The radiation damage of Amberlite LA-1 and LA-2 is negligible under these conditions (dose rate is 8.1×10^5 r/h, maximum total dose is 5×10^7 r).

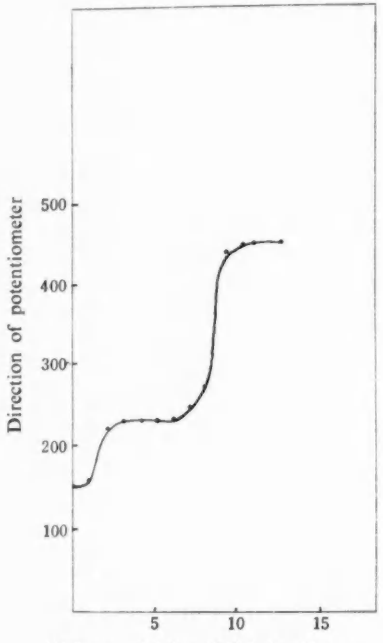

Fig. 9. Typical titration curve of Amberlite LA-1.

Summary

Uranium, protactinium and thorium are satisfactorily separated from each other by secondary amine extraction. Amberlite LA-1 in kerosene diluent is used as the extractant. Separation from hydrochloric acid solution is superior to that from systems using other acids. The acid

8) J. S. Fritz, A. U. Moye and M. J. Richard, *Anal. Chem.*, **29**, 1685 (1957).

dependency of the extraction coefficient by amine fairly resembles that of the distribution coefficient by anion exchange resin, but the former has a selectivity for uranium. Under the total dose of 5×10^{7} *r*., the radiation damage of Amberlite LA-1 is negligibly small. From these results, it is evident that there is a possibility of applying the amine extraction to the recovery of uranium-233 from reactor blanket fuel.

The authors wish to express sincere thanks to Dr. Toshio Nakai for his guidance.

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Studies on Seven-Membered Heterocyclic Compounds Containing Nitrogen. III. Reactions of 5-Benzyl-1-oxa-5-azaspiro(5, 2)octane

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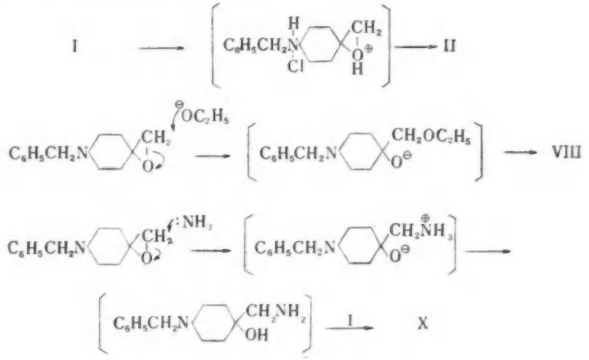
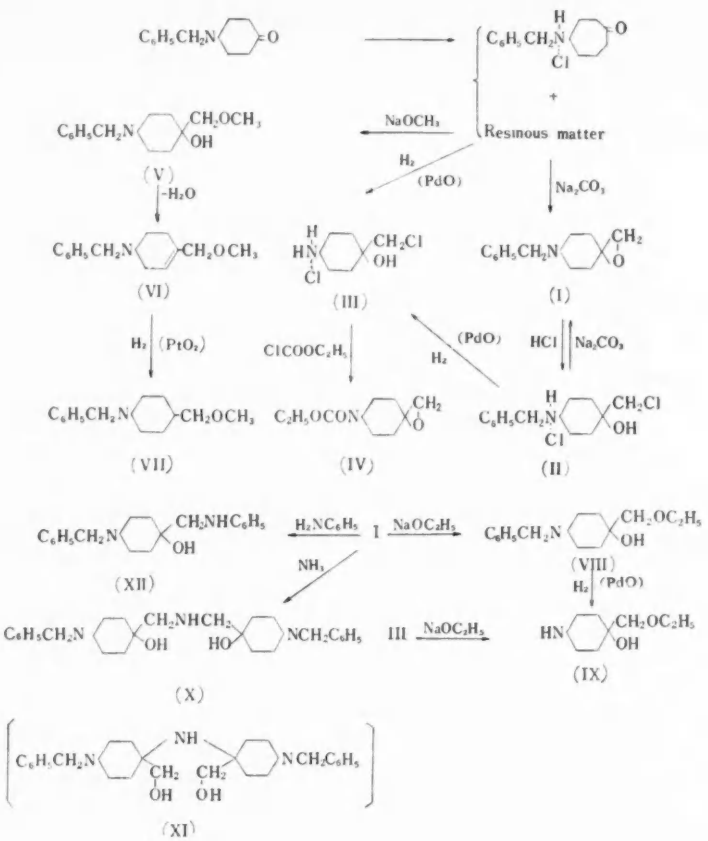
Previously[1] the author reported that 1-benzyl-1-azacycloheptan-4-one was obtained from 1-benzyl-1-azacyclohexan-4-one by ring enlargement and recrystallization as a hydrochloride, followed by the addition of alkali. The present study was undertaken in order to investigate an acidic resinous matter left in a considerable amount on evaporation of mother liquor of the recrystallization, and an epoxy compound was found out. Behaviors of the epoxy group to acid and base were examined.

After treatment of the resinous matter with alkaline water while hot, extraction with benzene yielded an oil, boiling at 119~121°C/0.45 mmHg (I). Infrared absorption spectrum showed that the oil was contaminated with a little ketonic substance even after several recrystallizations as a hydrochloride (II) and liberation by alkali. The oil afforded a sulfonic acid derivative[2] with sodium bisulfite, while 1-benzyl-1-azacycloheptan-4-one a normal addition product. The oil, if necessary, was further treated with 2, 4-dinitrophenylhydrazine and chromatographed on alumina, decolorizing carbon and magnesium sulfate[3]. The infrared absorption spectrum of the purified oil indicated characteristic two bands at 790 cm^{-1} and 895 cm^{-1}, which is presumably ascribed to the epoxy group. These two bands disappeared in the infrared absorption spectrum of such compounds derived by opening the epoxy group of I as VIII, X and XII. Judging from the nitrogen analysis and the infrared absorption spectrum, the purified oil, b. p. 114°C/0.43 mmHg, was considered as an epoxy compound, 5-benzyl-1-oxa-5-azaspiro(5, 2)octane, being isomeric with 1-benzyl-1-azacycloheptan-4-one[1].

Reduction of both the resinous matter and



1) S. Morosawa, This Bulletin, 31, 418 (1958).
2) W. M. Lauer and A. Hill, *J. Am. Chem. Soc.*, **58**, 1873 (1936).
3) R. P. Linstead, J. A. Elvidge and M. Whalley, "A Course in Modern Techniques of Organic Chemistry", Butterworths Scientific Publications, London, (1955), p. 6.



II in the presence of palladous oxide produced an identical substance, m. p. 183~184°C, which was assumed to be III. III afforded a picrolonate, m. p. 228~229°C (decomp.). III and ethyl chlorocarbonate in alkali medium gave an *N*-carbethoxy epoxy compound, b. p. 94~95°C/1 mmHg (IV). The resinous matter and sodium methoxide in absolute methanol gave an oil, b. p. 146~147°C/1 mmHg (V), which was readily dehydrated to an ethylenic compound, b. p. 126°C/0.5 mmHg (VI). VI was then reduced in the presence of platinum oxide to a saturated compound, b. p. 118~120°C/4.5 mmHg (VII). In the formations of II, III and V isomeric abnormal products[4] were not detected.

In view of these facts, it was clear that II was not a primary hydroxy type but a tertiary one, and that the epoxy group of I was opened, when made acidic, and thus I might exist in the resinous matter in the form of II. Ring opening of the epoxide group by the addition of hydrogen chloride was probably due to the normal way.

I and sodium ethoxide in absolute ethanol gave an oil, b. p. 143~144°C/5 mmHg (VIII), which on reduction in the presence of palladous oxide yielded an oil, b. p. 92~93°C/7.5 mmHg (IX). On the one hand, III also gave an oil, b. p. 94°C/7.5 mmHg by the action of sodium ethoxide, which was assumed to accord with IX. This was confirmed by mixed fusion of their picrolonates. It seemed reasonable, therefore, to assume that the addition of ethanol to the epoxy group would proceed as shown below. That the ethoxide anion attacked the methylene carbon and not the spiro carbon is probably due to the steric effect.

I and ammonia in ethanolic solution yielded a crystal, m. p. 142.5°C. Among possible structures corresponding to the crystal, formula X was most probable and the other, for instance XI, could not be constructed in practice into the molecular model owing to the steric interference. The reaction might proceed in the manner like above.

4) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

I and aniline gave a yellow oil, b. p. 202～203°C/0.2 mmHg (m. p. 79.5°C) (XII). This additional reaction also appeared to be the same as in the case of ammonia.

The infrared absorption spectra of VIII, X and XII exhibited characteristic peaks of the tertiary νOH at 1115 cm^{-1} [5].

Experimental

5-Benzyl-1-oxa-5-azaspiro(5, 2)octane (I).—A mixture of 52 g. of the resinous matter, 100 g. of sodium carbonate and 100 cc. of water was stirred for 5 hr. under heating at 70°C. An oily liberated substance was taken up in benzene and dried over potassium carbonate. Evaporation of benzene and rapid vacuum distillation in three batches gave 23 g. of crude epoxide, a colorless oil, b.p. 119～121°C/0.45 mmHg, and when not, much of the substance remained undistilled. (Found: N, 6.99%).

A mixture of 3 g. of the crude epoxide and an excessive saturated solution of sodium bisulfite was shaken vigorously for a short time. Crystals formed were filtered and recrystallized from dilute ethanol to yield 2.3 g. of colorless hexagonal prisms, m. p. 251.5°C (decomp.). It was very soluble in water and did not liberate any oil with acid or alkali.

Found: N, 4.36. Calcd. for $C_{13}H_{17}ON \cdot NaHSO_3$: N, 4.56%.

On the contrary, 1-benzyl-1-azacycloheptan-4-one gave a normal addition product, m.p. 155°C (decomp.). (Found: N, 4.40%).

A mixture of 2.7 g. of the crude epoxide, 0.8 g. of 2,4-dinitrophenylhydrazine, 0.5 cc. of concentrated hydrochloric acid and 30 cc. of ethanol was boiled on a water bath for two minutes and let stand overnight. Crystals formed were filtered and washed with a little amount of ethanol. The ethanolic solution was passed through Amberlite IRA-400 to remove the hydrochloric acid and evaporated to dryness under reduced pressure. The residual oil was chromatographed on a column packed (from top) with alumina, decolorizing carbon and magnesium sulfate[5] and eluted with dry benzene. The eluate was evaporated and vacuum distillation of the residue yielded 1.7 g. of a colorless oil, b. p. 114°C/0.43 mmHg. Infrared absorption spectrum of the oil showed no carbonyl band.

Found: N, 7.02. Calcd. for $C_{13}H_{17}ON$: N, 6.89%.

1-Benzyl-4-chloromethyl-4-hydroxy-1-azacyclohexane Hydrochloride (II).—Through a solution of the crude epoxide in absolute ether was passed dry hydrogen chloride to precipitate a white amorphous hydrochloride. Ether was decanted and the hydrochloride was recrystallized from methanol and ether to give a white crystalline powder. Because of its highly hygroscopic property, it could not be analyzed, but was assumed to be 1-benzyl-4-chloromethyl-4-hydroxy-1-azacyclohexane hydrochloride from the experiment described later. Treatment of the powder with alkaline water as above reformed the epoxide, but not pure.

5) 1-Methylcyclohexane-1-ol gives the peak of the tertiary νOH at 1117 cm^{-1}. H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, 75, 897 (1953).

4-Chloromethyl-4-hydroxy-1-azacyclohexane Hydrochloride (III).—(a) A solution of 5 g. of the acidic resinous matter in 70 cc. of water was reduced under normal temperature and pressure with 0.2 g. of palladous oxide as a catalyst until the theoretical amount of hydrogen had been absorbed. The catalyst was filtered off, and evaporation of water under reduced pressure left light yellow crystals, which were recrystallized from methanol and ether to yield 2 g. of colorless prisms, m. p. 183～184°C.

Found: C, 38.97; H, 7.13; N, 7.52. Calcd. for $C_6H_{13}ONCl_2$: C, 38.73; H, 7.04; N, 7.53%.

III formed a *picrolonate* by heating with a saturated ethanolic solution of picrolonic acid, which was recrystallized from ethanol to give yellow micro prisms, m. p. 228～229°C (decomp.).

Found: N, 15.61. Calcd. for $C_{16}H_{21}O_6N_5Cl_2$: N, 15.55%.

(b) A solution of 10 g. of II in 200 cc. of water was shaken in the hydrogen atmosphere with heating in the presence of 0.2 g. of palladous oxide as a catalyst until the theoretical amount of hydrogen had been absorbed. Light yellow needles were obtained after separation of the catalyst by filtration, followed by evaporation of water. The needles were recrystallized five times from methanol to give 2 g. of colorless prisms, m. p. 183.5～184°C in 30.7% yield, and this did not depress the melting point on admixture with the colorless prisms described above. (Found: N, 7.16%).

A *picrolonate* which derived from the prisms was also not depressed by mixing with the picrolonate mentioned above, m. p. and mixed m. p. 229°C (decomp.). (Found: N, 15.73%).

5-Carbethoxy-1-oxa-5-azaspiro(5, 2)octane (IV).—To a solution of 2 g. of III in 10 cc. of water, under stirring and cooling at below 5°C, a solution of 1.3 g. of ethyl chlorocarbonate in 10 cc. of ether and 5 cc. of 30% sodium hydroxide solution were gradually added during 1.5 hr., at such a rate that the two solutions were added simultaneously. After stirring for 15 min. the water layer was separated and extracted three times with a portion of 30 cc. ether each. Combined ethereal solution was dried over potassium carbonate. After evaporation of ether, the vacuum distillation gave 1.4 g. of a colorless oil, b. p. 94～95°C/1 mmHg in 58% yield.

Found: N, 7.29. Calcd. for $C_9H_{15}O_3N$: N, 7.56%.

1-Benzyl-4-methoxymethyl-4-hydroxy-1-azacyclohexane (V).—A solution of 14 g. of the resinous matter in 40 cc. of absolute methanol was mixed with a solution of 7 g. of sodium dissolved in 100 cc. of absolute methanol. The resultant mixture was boiled under reflux for 8 hr. After that, 5 cc. of water was added and filtered from the sodium chloride present. The sodium chloride was washed with methanol. Combined methanolic solution was evaporated to leave an oily substance, which was taken up in ether, washed twice with a 10% solution of potassium carbonate and dried over potassium carbonate. Ether was removed and the residual oil was distilled in vacuo to give 7.8 g. of a colorless oil, b. p. 146～147°C/1 mmHg.

Found: N, 5.94. Calcd. for $C_{14}H_{21}O_2N$: N, 5.95%.

1-Benzyl-4-methoxymethyl-1-azacyclohex-3-ene (VI).—A mixture of 4.3 g. of V and 6.1 g. of β-naphthalenesulfonic acid was heated for 15 min. on a water bath under reduced pressure (water pump), and then for 1 hr. at 170°C. After cooling, 100 cc. of 10% sodium hydroxide solution was added, extracted in ether and dried over potassium carbonate. Ether was expelled and the vacuum distillation yielded 2.2 g. of a colorless oil, b. p. 126°C/0.5 mmHg. in 56.7% yield, which on standing turned pink immediately.

Found: C, 76.75; H, 8.62; N, 6.55. Calcd. for $C_{14}H_{19}ON$: C, 77.38; H, 8.81; N, 6.45%.

1-Benzyl-4-methoxymethyl-1-azacyclohexane (VII).—A solution of 1.1 g. of freshly distilled VI in 50 cc. of methanol containing 0.6 cc. of concentrated hydrochloric acid was reduced in the presence of platinum oxide as a catalyst and the theoretical amount of hydrogen was consumed. After removal of the catalyst by filtration, methanol was distilled off and the residue was made alkaline. Oil thereby liberated was taken up in ether and dried over potassium carbonate. The ether was removed to leave an oil, which on vacuum distillation gave 0.25 g. of a colorless, fluid oil, b. p. 118~120°C/4.5 mmHg.

Found: C, 76.23; H, 9.94; N, 6.31. Calcd. for $C_{14}H_{21}ON$: C, 76.67; H, 9.65; N, 6.39%.

1-Benzyl-4-ethoxymethyl-4-hydroxy-1-azacyclohexane (VIII).—A solution of 4 g. of I in 10 cc. of absolute ethanol was mixed with a separately prepared solution of 1.5 g. of sodium in 30 cc. of absolute ethanol and the whole was boiled under reflux for 8 hr. After cooling, 2 cc. of water was added and evaporated under reduced pressure to leave an oil, which was taken up in ether, washed twice with a dilute potassium carbonate solution and dried over potassium carbonate. Oil left on evaporation of ether was distilled in vacuo to yield a colorless oil boiling at 128~136°C/0.5 mmHg, which was redistilled to give 2.5 g. of the oil, b. p. 143~144°C/5 mmHg, in 50.3% yield.

Found: N, 5.77. Calcd. for $C_{15}H_{23}O_2N$: N, 5.62%.

4-Ethoxymethyl-4-hydroxy-1-azacyclohexane (IX).—(a) A solution of 2.5 g. of VIII in 50 cc. of water containing 1 cc. of concentrated hydrochloric acid was reduced with heating and in the presence of 0.1 g. of palladous oxide as a catalyst until the theoretical amount of hydrogen had been absorbed. After separation of the catalyst by filtration, a residue left on evaporation of water was dissolved in 10 cc. of water and neutralized with potassium carbonate. A further addition of 2 g. of sodium hydroxide liberated an oil, which was extracted in ether and dried over potassium carbonate. Evaporation of ether and distillation in vacuo gave 0.5 g. of an oil, b. p. 92~93°C/7.5 mmHg in 31% yield.

Found: N, 8.77. Calcd. for $C_8H_{17}O_2N$: N, 8.82%.

IX formed a *picrolonate*, m. p. 209°C (decomp.), which was recrystallized twice from ethanol to yield yellow micro prisms, m. p. 216~217°C (decomp.).

Found: N, 16.31. Calcd. for $C_{18}H_{25}O_7N_5$: N, 16.54%.

(b) A solution of 1 g. of III in 5 cc. of absolute ethanol was mixed with a separately prepared solution of 1 g. of sodium dissolved in 15 cc. of absolute ethanol and the whole was boiled under reflux for 8 hr. After cooling, 2 cc. of water was added and filtered from any solid, which was washed with ethanol. A tan oily substance left on evaporation of ethanol was treated as before to give 0.5 g. of an oil, b. p. 94°C/7.5 mmHg (Found: N, 8.73%).

A *picrolonate* of the oil, m. p. 216~217°C (decomp.) was not depressed on admixture with that described before. (Found: N, 16.37%).

4-Anilinomethyl-1-benzyl-4-hydroxy-1-azacyclohexane (XII).—A mixture of 4.2 g. of I and 3.3 g. of freshly distilled aniline was boiled under reflux for 1.5 hr. Excessive aniline was removed under reduced pressure to leave a colored residue. Vacuum distillation of the residue gave 3.7 g. of a light yellow viscous oil boiling at 202~203°C/0.2 mmHg in a 60.5% yield. The oil gradually crystallized on standing and was recrystallized from cyclohexane and benzene in light creamy plates, m. p. 79.5°C.

Found: C, 76.70; H, 8.29; N, 9.44. Calcd. for $C_{19}H_{24}ON_2$: C, 76.99; H, 8.16; N, 9.45%.

XII afforded a *picrate*, m. p. 177.5°C (from ethanol).

Found: N, 14.55. Calcd. for $C_{19}H_{24}ON_2 \cdot (C_6H_3O_7N_3)_2$: N, 14.85%.

Bis-(4-benzyl-1-hydroxy-4-azacyclohexylmethyl)-amine (X).—A solution of 2 g. of I in 10 cc. of 99% ethanol was saturated with ammonia at 0°C and let stand for a week at room temperature. An ether insoluble substance left on evaporation of ethanol was recrystallized from dilute ethanol after treating with decolorizing carbon to give 0.6 g. of colorless scales, m. p. 142.5°C in a 30% yield.

Found: C, 73.50; H, 8.96; N, 9.99. Calcd. for $C_{26}H_{37}O_2N_3$: C, 73.72; H, 8.80; N, 9.92%.

Both *picrate*, m. p. 225°C (decomp.) and *picrolonate*, m. p. 247°C (decomp.) were insoluble and difficult to recrystallize from any common solvent.

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Kinetic Study on Isomerization of Anthranol to Anthrone

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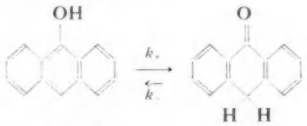
Only a few studies concerning the physical and chemical properties of anthranol have been reported in literature. K. H. Meyer[1] found in 1911 that in organic solvents anthranol turns to anthrone and after a long time a chemical equilibrium between these substances is established. Bäckström et al.[2] pointed out an iodine titration method for the analysis of anthranol. Le Fèvre et al.[3] investigated the dielectrical properties of the same substance, but its purity was not satisfactory enough to determine the dielectric constant of the solutions.



Anthranol Anthrone

The authors have established the best condition for the preparation of anthranol and measured the dipole moments in several organic solvents[4].

In this paper, the authors present the methods of measuring the velocity constants of the isomerization of anthranol to anthrone by the analytical and dielectrical techniques and the calculated values of the activation energies of the reaction.

Experimental

Preparation of Anthranol.—Improving the original procedures of Meyer[1] and Bäckström et al.[2], the authors have established the best method of preparation of pure anthranol and reported the findings in this Bulletin[4].

Measurements of Velocity Constants of the Isomerization by Iodometry.—Bäckström et al. determined the purity of anthranol by iodometric analysis. This suggests that the method may also be used for the measurement of isomerization velocity, because one mole of anthranol reacts exactly with one mole of iodine in some solvents, while anthrone does not react with iodine at all. It has been found that methanol and ethanol were suitable solvents for the measurement of isomerization velocity.

In a stream of nitrogen, 1.0 g. of freshly prepared anthranol was dissolved into 200 cc. of solvent keeping the temperature constant. After appropriate time, 10 cc. of the solution was poured into 5 cc. of 0.1 N iodine-potassium iodide aqueous solution. After a few minutes the remaining iodine was titrated with 0.1 N sodium thiosulfate solution, and thus the content of anthranol in the solution was obtained directly. These operations were repeated until an equilibrium of the reaction was attained.

Dielectrical Measurement.—The authors have already measured the apparent dipole moments of anthranol in several organic solvents at 6 and 15°C[4]. At these temperatures, isomerization velocities are so small that anthranol in solvents safely remains unchanged during the measurements.

When the temperature is raised, the reaction velocity of isomerization becomes greater and it becomes impossible to get the real value of dipole moment of anthranol. A kinetic study of isomerization, on the other hand, becomes possible even at elevated temperatures.

Dielectric constants of solutions (in benzene and toluene) at several temperatures were measured several times until they reached maximum values. Although it is necessary also to measure the densities of solutions at every time of measurements of dielectric constants, this procedure is very troublesome. Hence, in this paper, it was assumed that the density of solutions remained constant during the reaction.

Results and Discussion

Iodometry.—First of all, it was assumed that the reaction is reversible and of the first order, so that

$$\frac{dx}{dt} = k_+(a_0 - x) - k_-(a_0' + x) \qquad (1)$$

where x is the amount of changed anthranol at the time t, a_0 and a_0' are the initial amounts of anthranol and anthrone expressed in molar fraction, and k_+ and k_- are the velocity constants of normal and reverse reactions, respectively. As the purity of the anthranol was about 98%,

$$a_0 \fallingdotseq 1 \quad \text{and} \quad a_0' \fallingdotseq 0$$

and then

$$K = \frac{k_+}{k_-} \fallingdotseq \frac{a_\infty}{1 - a_\infty} \qquad (2)$$

where K is the equilibrium constant and a_∞ is the value of x at the equilibrium $(dx/dt = 0)$.

1) K. H. Meyer, *Ann.*, **379**, 37 (1911).
2) H. Bäckström and H. Beatty, *J. Phys. Chem.*, **35**, 2549 (1930).
3) C. L. Angyl and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1950**, 562.
4) K. Nukada and Y. Bansho, This Bulletin, **26**, 454 (1953).

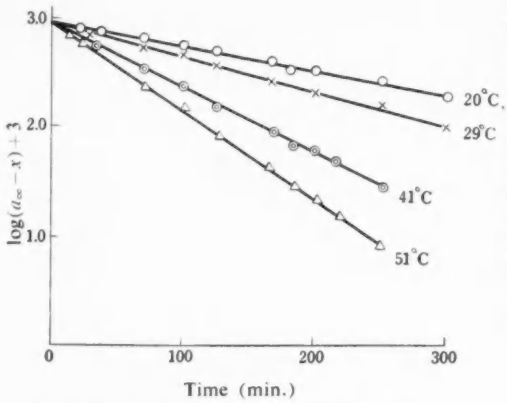


Fig. 1. Kinetics in methanol by iodometry.

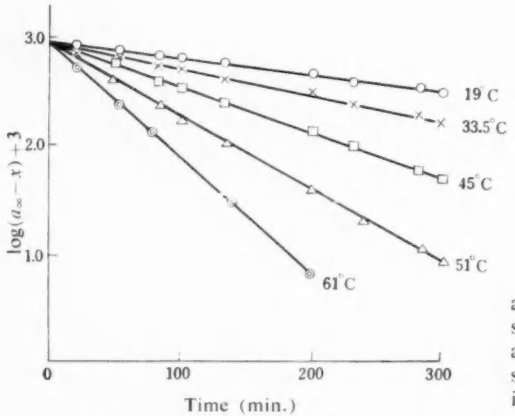


Fig. 2. Kinetics in ethanol by iodometry.

TABLE I. THE VELOCITY CONSTANTS OF ISOMERIZATION

Temp., °C	In methanol k_+	In ethanol k_+
20	0.0050	0.0032
29	0.0063	
36		0.0050
41	0.0125	0.0059
45	0.0137	0.0079
51	0.0165	0.0149
61	0.0256	0.0211

From Eqs. 1 and 2, the next equation is obtained.

$$k_+ + k_- = 1/t \ln [a_\infty/(a_\infty - x)] \quad (3)$$

From Eqs. 2 and 3, the value of k_+ can be obtained. In Figs. 1 and 2, $\log(a_\infty - x)$ are plotted against t at between 20~60°C in methanol and ethanol solutions, respectively. Since rectilinear relationships between $\log(a_\infty - x)$ and t were observed, it is reasonable to assume that the reaction of isomerization is of the first order. The calculated values of k_+ are shown in Table I.

According to Arrhenius' equation, the authors plotted the values of $\log k_+$ against the reciprocal of absolute temperature $(1/T)$ as shown in Fig. 3 and calculated the activation energies of the isomerizations of anthranol in methanol and ethanol. Anthranol isomerizes faster in methanol than in ethanol and the obtained values of activation energies are 5.8 and 12.4 kcal./mol. in methanol and ethanol, respectively. This might be due to the fact that ethanol is stronger in basisity than methanol.

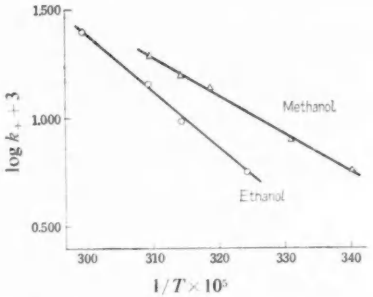


Fig. 3. Measurements of activation energies by iodometry.

The times required for the complete disappearance of fluorescence in diluted anthranol solutions were ca. 50 and 6.5 hr. in ethanol and methanol, respectively[4]. These times are supposed to depend upon the velocities of isomerization.

Dielectrical Measurement.—The only measurable quantity with dielectrical measurement is the time dependency of the dielectric constant of solutions at various temperatures. In order to obtain the velocity constants from these measurable quantities, some assumptions are made.

First of all, it was assumed that

$$p_{12}(t) = (1-y)p_1 + yp_2(t) \quad (4)$$

where $p_{12}(t)$, p_1 and $p_2(t)$ are the specific molecular polarizations of solution, solvent and solute, respectively, and y is the weight fraction, of solute. The molecular polarization of solute $P_2(t)$ is obtained by substituting the following Eqs. 5—7 into Eq. 4.

$$p_{12}(t) = 1/d_{12} \times (\varepsilon_{12}(t) - 1)/(\varepsilon_{12}(t) + 2) \quad (5)$$

$$p_1 = 1/d_1 \times (\varepsilon_1 - 1)/(\varepsilon_1 + 2) \quad (6)$$

$$p_2 = P_2(t)/M \quad (7)$$

where $\varepsilon_{12}(t)$, ε_1 and d_{12}, d_1 are dielectric constants and densities of solution and solvent, respectively, and M is a molecular weight of

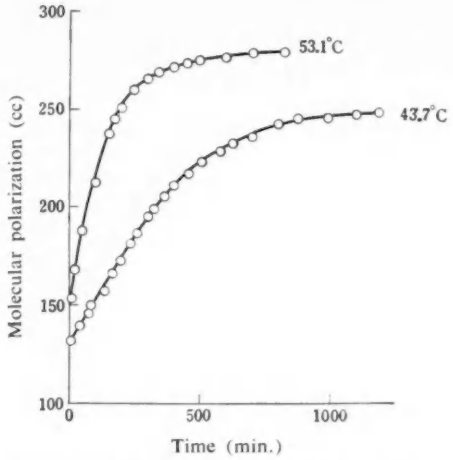


Fig. 4. The change of molecular polarization in benzene.

solute. $p_{12}(t)$, $p_2(t)$, $P_2(t)$ and $\varepsilon_{12}(t)$ mean that these quantities are functions of time. In Fig. 4, $P_2(t) \sim t$ curves are shown.

If the reaction is of the first order, Eq. 3 leads

$$\exp(-kt_i) = 1 - x(t_i)/a_\infty \tag{8}$$

where $k = k_+ + k_-$ and $i = 1, 2, 3, \ldots\ldots, N$ (N is the number of measurement). If it is possible to measure $x(t)$, the two unknown parameters k and a_∞ in Eq. 8 can be determind by the statistical method of least square, and then with Eq. 2 the normal velocity constant k_+ can be calculated. In the dielectrical measurement, however, $x(t_i)$ can not be obtained directly but only $P_2(t)$ can be measured. So it is necessary to combine the above quantities using a further assumption as follows:

$$P_2(t) = P_L[1 - x(t)] + P_N x(t) \tag{9}$$

where P_L and P_N are the molecular polarizations of pure anthranol and pure anthrone, respectively, and both are unknown parameters. From Eq. 9, it is obtained the following equations.

$$x(t) = (P_2(t) - P_L)/(P_N - P_L) \tag{10}$$

With $t = \infty$ the authors have $x = a_\infty$, so that

$$a_\infty = (P_2(\infty) - P_L)/(P_N - P_L) \tag{11}$$

where $P_2(\infty)$ means the saturated $P_2(t)$ value. Substituting Eqs. 10 and 11 to Eq. 8, it is obtained

$$\exp(-kt_i) = (P_2(\infty) - P_2(t_i))/(P_2(\infty) - P_L) \tag{12}$$

Eq. 12 includes two unknown parameters (k and P_L) but they can be obtained by the statistical method of least square. In the present case the velocity constant of the reverse reaction is found to be very small compared with that of the normal reaction*. Therefor, k_+ is almost equal to k and the final equation is obtained.

$$k_+ \fallingdotseq k = \frac{\sum_i \ln(P_2(\infty) - P_2(t_i)) \sum_i t_i/N - \sum_i t_i \ln(P_2(\infty) - P_2(t_i))}{\sum_i t_i^2 - (\sum_i t_i)^2/N} \tag{13}$$

If Arrhenius' equation is also valid in this cace, the curve $\ln k_+ \sim 1/T$ should be linear and the results agree quite well with this requirement (Fig. 5). Activation energies, obtained from Fig. 5 are listed in Table II. These values are of the same order as those obtained in methanol and ethanol solutions by the iodine titration method. It is important to notice that the potential barrier between two isomers is rather small so that the isomerization can occur very easily.

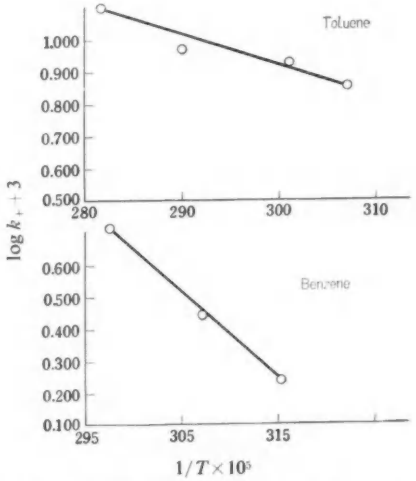


Fig. 5. Measurements of activation energies by dielectrical method.

TABLE II. THE ACTIVATION ENERGIES OF ISOMERIZATION MEASURED IN SEVERAL ORGANIC SOLVENTS

Solvent	Method of measurement	Activation energies kcal./mol.
Methanol	Iodometry	5.8
Ethanol	Iodometry	12.4
Benzene	Dielectrical method	12.2
Toluene	Dielectrical method	4.8

The authors could not find common solvents suitable to measure the velocity constant for

* The authors measured the molecular polarization of anthrone in benzene and toluene and ascertained that $P_2(t)$, in this case, maintained its initial value even after a long time, i. e. k_- was almost equal to zero.

both the analytical and dielectrical methods for the following reasons: methanol and ethanol are polar substances and not suitable for the dielectrical measurement, while benzene and toluene are immiscible with water making iodometry titration impossible.

Conclusion

Pure anthranol was prepared and its isomerization to anthrone was studied by analytical and dielectrical methods. The reaction was found to be of the first order and the observed heat of activations were 5.8, 12.4, 12.2 and 4.8 kcal./mol. in methanol, ethanol, benzene and toluene, respectively. These small values mean that anthranol isomerizes easily in these solvents.

Sincere thanks are tendered to Dr. Y. Mashiko of this Institute for his valuable discussion. The authors also appreciate the help rendered by Mr. Kuang Lieh Huang in performing a part of these experiments.

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β-Hydroxyleucine. I. Synthesis by Means of Copper Complex and Separation of the Diastereomeric Racemates

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β-Hydroxyleucine has recently been found by Kenner and Sheppard[1] to be a constituent of an antibiotic (I. C. I. No. 13959), which is unusually active against infection of *Trypanosoma congolense*, and they assigned the structure D- or L-threo isomer to the natural product. This is, as they stated, the first time that β-hydroxyleucine has been obtained from natural sources.

A survey of the literature indicates that the procedures reported hitherto for the synthetic preparation of this amino acid are rather complicated and that yields are poor.

It was synthesized by Abderhalden for the first time from isocaproic acid through isopropyl-acrylic acid in an overall yield of 7%[2], by Wieland and coworkers by adding isobutyraldehyde into a melting mixture of glycine and potassium hydroxide in a 20% yield[3], and by Buston and Bishop by hydroxybromination of isopropylacrylic acid in a 12% yield[4]. The authors have succeeded in preparing β-hydroxyleucine as a diastereomeric mixture in a high yield by the copper complex method[5] by which already threonine[5], serine[6] and β-hydroxy-β-methylaspartic acid[7] were successfully synthesized.

Glycine copper complex was allowed to react in the presence of potassium or sodium hydroxide with isobutyraldehyde. The reaction mixture was treated with aqueous ammonia and the copper was removed by means of an ion exchange resin (Dowex 50). The product thus freed from copper was found to contain no by-product but a trace of unreacted glycine by paperchromatographic analysis. Having two asymmetric carbons in α- and β-positions, β-hydroxyleucine has two diastereomeric racemates. The separation of these diastereomers was effected by utilizing the different solubility of their sodium salts in absolute ethanol. The amino acid (A) derived from the insoluble salt showed a decomposition point of 240~241°C and that of (B) from the soluble salt 255~256°C. Although Buston and Bishop[4] reported that β-hydroxyleucine is separable into two isomers with m. p. 240 and 209°C, the authors could never obtain the latter. Paperchromatography in a solvent system of methyl ethyl ketone—*n*-butanol—concentrated ammonia—water (3 : 5 : 1 : 1) permits the definite separation of these

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2) E. Abderhalden, *Z. physiol. Chem.*, **251**, 164 (1938).
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isomers. (A-form, $R_f=0.49$; B-form, $R_f=0.32$). The ratio of A- to B-form obtained was 1.8～2.8 as measured by the ninhydrin method[8]. These results are shown in Table I. In comparison with threonine it may be assumed that A- and B-forms correspond to the threo and erythro-forms, respectively. The definite assignment of structure is under way and will be reported later.

TABLE I. YIELDS AND RATIOS OF THE DIASTEREOMERS OBTAINED WITH VARIOUS CATALYSTS

Catalyst	Yield	Form A	Form B	Form A/Form B
KOH	76%	63.7%	36.3%	1.8
NaOH	69%	73.5%	26.5%	2.8
Na_2CO_3	Trace	—	—	—
$H_2N-CH_2-CH_2-NH_2$	Trace	—	—	—

Experimental

Isobutyraldehyde.—The aldehyde was prepared according to Whitmore's method[9] with slight modification.

β-Hydroxyleucine.—In a 500 cc. flask, 30 g. of freshly distilled isobutyraldehyde was added to a suspension of 23 g. of copper complex of glycine in a solution of 8 g. of potassium hydroxide (or 6 g. of sodium hydroxide) in 40 cc. of water. The suspension was swirled for a few minutes, and then placed in a refrigerator overnight. The reaction mixture was transferred to a mechanical shaker and shaken at room temperature for 5 hr. Two hundred cubic centimeters of water and 170 cc. of concentrated aqueous solution of ammonia were added and the resulted solution was filtered. The filtrate was passed through a column of Dowex 50 which had previously been converted into the ammonium form. Then the column was eluted with 5 N aqueous solution of ammonia, and the eluate was collected until no further positive ninhydrin reaction.

The effluent was concentrated under reduced pressure until the crystallization of β-hydroxyleucine began, and then about three volumes of ethanol were added. After being kept in a refrigerator overnight, the crystals of β-hydroxyleucine were collected, washed with ethanol, and dried in vacuo. When potassium hydroxide was used as catalyst, the yield was 22 g. (76%); and in the case of sodium hydroxide the yield was 20 g. (69%).

The reaction product was contaminated with a small amount of unreacted glycine and it was a mixture of two racemic diastereoisomers.

Synthetic β-hydroxyleucine, when recrystallized from water by the addition of ethanol after decolorization with charcoal, showed an m.p. of 240～241°C (decomp.).

Found: C, 48.55; H, 9.07; N, 9.50. Calcd. for $C_6H_{13}NO_3$: C, 48.96; H, 8.90; N, 9.52%.

Determination of the ratio of A- to B-form was carried out by separating them on paperchromatogram in the solvent system mentioned above and by measuring the optical density of 50% ethanol of each spot treated with ninhydrin.

Separation of the Diastereomeric Racemates.—Fourteen and seventenths grams of β-hydroxyleucine was added to a hot solution of sodium ethylate prepared from 2.3 g. of sodium and 50 cc. of absolute ethanol. The suspended mixture was refluxed with agitation for an hour, and placed at room temperature overnight. The mixture was filtered to remove the sodium salt of Form A, and the separeted sodium salt of Form A was added to 50 cc. of ethanol. The mixture was refluxed for an hour and the precipitate was collected and washed with ethanol.

The collected sodium salt of Form A was dissolved in 200 cc. of water and the solution was passed through a column of Amberlite-IRC 50 which had been converted into the H-form. Water was passed through the column until the effluent became ninhydrin negative. The aqueous effluent containing free β-hydroxyleucine (Form A) was concentrated under reduced pressure to a low bulk. Excess ethanol was added, and the resulting precipitate was collected by filtration after storage in a refrigerator overnight and washed with ethanol. The yield was 10 g.

Recrystallization of the product was effected from water by the addition of ethanol after decolorization with a small amount of charcoal. The product, when chromatographed on paper, revealed only a single ninhydrin-positive spot which was identical with Form A, and it showed an m.p. of 240～241°C (decomp.).

Found: C, 48.91; H, 8.72; N, 9.60. Calcd. for $C_6H_{13}NO_3$: C, 48.96; H, 8.90; N, 9.52%.

On the other hand the filtrate, namely, the ethanol solution of sodium salt of Form B was treated in the same manner as described above and its free amino acid was obtained. The yield was 2.3 g. and m.p. 255～256°C (decomp.).

Found: C, 48.95; H, 8.75; N, 9.60. Calcd. for $C_6H_{13}NO_3$: C, 48.96; H, 8.90; N, 9.52%.

Reduction of β-Hydroxyleucine with Hydriodic Acid.—In a sealed tube a mixture containing 0.05 g. of β-hydroxyleucine, 0.02 g. of red phosphorous and 3 cc. of hydriodic acid ($d=1.60$) was heated for 10 hr. at 150°C. By paperchromatographic analysis of the reaction product it was confirmed that most of the starting material had been reduced to leucine, but a part of β-hydroxyleucine remained unchanged in the reaction mixture. The paperchromatograms also showed three ninhydrin-positive spots of glycine, and unidentified substances with R_f-values 0.22 and 0.00.

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The Kinetic Study of Surface-chemical Reactions at Extremely Low Pressures. V. The Thermal Reaction between Water Vapor and a Tungsten Filament. Part V

By Takuya HAMAMURA

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In previous papers[1-4] of this series the reaction of water vapor with tungsten in the 1270 to 1950° K temperature range was presented. Here the data for this reaction from 1950 to 2460° K are given and discussed. The division into two temperature ranges is done for convenience in discussing the result. Below 1950° K a blue deposit having a mean apparent composition of $WO_{2.8}$ is produced on the wall of the vessel. Above 1950° K the ratio O/W of the deposit increases with the rise of the temperature and a colorless deposit is formed at higher temperatures.

Experimental

The apparatus was the same as that used in previous experiments. Tungsten filaments, 0.114mm. in diameter and 56mm. long, were used for determining the reaction rate and the composition of the reaction product. Procedures of measuring the reaction rate and determining the composition of the reaction products have been described previously. The two-filament method was not used to obtain the reaction probability owing to the too severe influence of hydrogen pressure on the reaction rate. The temperature of the reaction vessel remained at room temperature throughout the experiments.

Uptake of oxygen by the deposit was studied as follows. After the deposit had been produced, water vapor was removed from the vessel by cooling water reservior 1 in Fig. 1* with dry ice and a definite amount of oxygen was introduced into the vessel through cock 12 after the boiler of diffusion pump 7 was cooled. Then the vessel was heated in an electric furnace and the pressure decrease was measured by a McLeod manometer.

Desorption of a permanent gas from the deposit was studied as follows. After the deposit had been produced, water vapor was removed from the vessel in the manner mentioned above. The vessel was then heated in an electric furnace and the permanent gas given off was transferred into the glass balloon by diffusion pump 7. The pressure was measured by a McLeod manometer.

Results and Discussion

Reaction Rate.—Reaction rates were determined from 30×10^{-5} to 103×10^{-5} mmHg initial pressures of water vapor under various pressures of hydrogen in the vessel. It was found that the reaction rate decreased with the increase of hydrogen pressure more steeply as the temperature rose or the pressure of the water vapor decreased in a manner similar to that observed below 1950° K. The cause of decrease of the rate was studied by the following experiment. Two filaments of the same length** and diameter were heated in water vapor of the same initial pressure separately for the same interval of time with the same current under different pressures of hydrogen. The amount of hydrogen produced and the increment of resistance of the respective filaments were determined. Results for 1.5 amp. heating current (about 2350° K) are given in Table VI***. Increments of the resistance are almost the same for two filaments even though the amounts of hydrogen are considerably different. Therefore, it is apparent that the decrease is not caused by the retardation of the reaction of water vapor with tungsten by hydrogen.

The reaction probability at a definite temperature was evaluated from the reaction rate at zero pressure of hydrogen obtained by extrapolating back the rate vs. hydrogen pressure curve to zero pressure of hydrogen. Values of reaction probabilities at 60×10^{-5} mmHg of water vapor are given in Table VII. A probability at 1890° K is also given for comparison. These values are not free from the end effect of the filament.

Composition of Deposit.—Results obtained are given in Table VIII. It is obvious that the ratio O/W of the deposit increases with the rise of the temperature, whereas it decreases with the increase of the hydrogen pressure. Properties of deposits are as follows.

1) Deposits having ratio values O/W smaller than 3 appeared blue in transmitted light,

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* Fig. 1 is presented in the first paper of this series.

** Filaments, 12.8 cm. long, were used for this experiment.
*** Tables in the present paper are numbered after those of previous papers.

TABLE VI

Expt. No.	Heating time min.	Initial press. of H_2O mmHg$\times 10^5$	Press. of H_2 in vessel mmHg$\times 10^4$	Amount of H_2 produced mol.$\times 10^5$	Initial resist. at 25°C ohm	Increment of resist. ohm
1	50	91.0	5.5	1.97	1.171	0.033
1'	50	91.0	62.5	1.40	1.164	0.032
2	120	56.5	2.4	2.02	1.194	0.052
2'	120	56.5	18.0	0.96	1.203	0.050

TABLE VII. REACTION PROBABILITIES

Temp. of filament (°K)	1890	2000	2100	2200	2300
k	7.7×10^{-3}	1.3×10^{-2}	1.7×10^{-2}	2.5×10^{-2}	3.0×10^{-2}

TABLE VIII

Filament temp. °K	Initial press. of H_2O mmHg$\times 10^5$	Press. of H_2 in vessel mmHg$\times 10^5$	Net weight loss of filament mol.$\times 10^6$	Amount of H_2 produced mol.$\times 10^5$	Composition in WO_x	Gas mass No., product %
2000	103	26	7.85	2.26	$WO_{2.88}$	
2000	103	108	8.26	2.35	$WO_{2.85}$	
2110	58	21	4.17	1.32	$WO_{3.16}$	
2110	58	82	4.44	1.34	$WO_{3.01}$	
2110	103	19	6.95	2.10	$WO_{3.02}$	
2210	60	22	3.93	1.37	$WO_{3.48}$	
2310	66	22	3.38	1.36	$WO_{4.03}$	28 1.2% 32 0.4%
2310	66	66	3.39	0.99	$WO_{2.93}$	28 0.6% 32 0.6%
2310	103	37	5.27	2.02	$WO_{3.82}$	
2310	103	91	6.47	2.04	$WO_{3.15}$	
2430	60	18	3.36	1.31	$WO_{3.90}$	28 2.3% 32 1.2%
2430	60	46	2.88	8.84	$WO_{3.07}$	
2460	104	32	5.16	2.05	$WO_{3.98}$	

whereas those having ratio values greater than 3 appeared colorless.

2) The deposition of a colorless product revealed a bleaching action upon the blue deposit, that is, when the colorless product was deposited on the blue deposit the blue color faded gradually with the accumulation of the colorless deposit.

3) When 100×10^{-5} mmHg of oxygen was admitted to the blue deposit, oxygen was hardly taken up at all at room temperature, but it was taken up swiftly at 200°C with fading of the blue color.

4) When the blue and the colorless deposits were heated separately in high vacuum at 300°C for two hours, the desorption of a permanent gas and the change of the color were not observed in either case.

The bleaching action of the colorless product upon the blue deposit may be explained by making an assumption that besides the reaction between water vapor and tungsten, the thermal decomposition of water vapor takes place with an increasing rate with the rise of the temperature and oxygen thus produced reacts with the blue deposit to make it colorless. Although the reduction of the deposit by hydrogen must take place at the same time, so long as the oxidation rate predominates over the reduction rate the colorless product is produced. It is shown experimentally that the blue deposit takes up oxygen to become colorless.

It has been stated[4] that the deposit produced below 1950°K has the ratio value O/W of 2.8. On the other hand, at temperatures above 1950 °K the ratio value was found to increase with the rise of the temperature to become greater than 4. The ratio value may increase owing to the formation of a higher oxide or may appear to increase by the production of hydrogen, not being accompanied by the weight loss of the filament, because the ratio value is determined by the amount of hydrogen produced and the weight loss of the filament. The presence of a higher oxide than tungsten trioxide has not been reported in literature. If the deposit was composed of a peroxide, oxygen or hydrogen peroxide would be generated when the deposit was dissolved in sulfuric acid or in aqueous solution of sodium hydroxide. However, the oxygen

evolution was not observed at all and the hydrogen peroxide formation was not detected by luminol[5]. Peroxytungstic acids[6] have been reported by some investigators, but these acids are described as being unstable and as decomposing with the evolution of oxygen by heating. Therefore, it is obvious that the colorless deposit is not composed of these acids. The colorless deposit is composed of tungsten trioxide.

Thermal decomposition of water vapor has been assumed to explain the bleaching action of the colorless product, but if all the oxygen produced reacts with the filament to form tungsten trioxide, the ratio value can not become greater than 3. It is necessary for the ratio value to become greater than 3 that oxygen be consumed by another process than the reaction with the filament. The following processes may be considered for such consumption.

1) Oxygen leaves the reaction vessel to be introduced into the glass balloon. 2) Oxygen produces hydrogen peroxide to be caught by the trap cooled with liquid nitrogen. 3) Oxygen is taken up by the wall of the apparatus or by the deposit on the wall of the vessel.

Results of the analysis by the mass spectrometer are given in Table VIII. It is evident that the amount of oxygen introduced into the balloon is too little to explain the observed ratio value. Hydrogen peroxide[7,8] has been reported to be produced when the water vapor contacts with a Nernst tube at a high temperature or when atomic hydrogen combines with oxygen on a wall cooled with liquid oxygen. Therefore, hydrogen peroxide may be produced in the reaction of water vapor with the tungsten now being studied. The formation of hydrogen peroxide was studied by the following experiment; after a filament was heated at 2310°K in 60×10^{-5} mmHg of water vapor for two hours, the filament and the boiler of diffusion pump 7 were cooled and air was introduced into the apparatus to an atmospheric pressure. Trap 6 was then detached from the apparatus, warmed to room temperature and a luminol reagent was dropped in it within a dark room to detect hydrogen peroxide by its luminescence. As a result, hydrogen peroxide was not detected by this experiment although about 2×10^{-6} mol. of hydrogen peroxide must be produced if the observed ratio value is ascribed to the formation of hydrogen peroxide. A blank test revealed that about 2×10^{-7} mol. of hydrogen peroxide could be detected.

The fact that a permanent gas was not given off from the deposit at 300°C suggested that oxygen had not been physically adsorbed at all or that it had been chemisorbed by the wall of vessel and/or by the deposit. The uptake of oxygen by the wall of the apparatus was studied by carrying out an electrodeless discharge in oxygen within the vessel. The discharge vessel was 30 mm. in diameter and 130 mm. long. The vessel was connected with a trap cooled with liquid nitrogen and the pressure was measured with a McLeod manometer. The electrodeless discharge was carried out by placing the vessel in a coil through which a high frequency current flowed. After evacuating and degassing the apparatus, about 0.2 mmHg of oxygen was introduced into the apparatus. Then the discharge was carried out for two minutes, and the pressure was measured again. Thus, the oxygen pressure was measured every time after the two-minute discharge. The uptake of oxygen by the tungsten trioxide deposit was studied similarly by using a vessel whose wall had been covered with tungsten trioxide deposit formed by heating a tungsten filament mounted along the axis of a vessel in oxygen. As a result, it was found that the tungsten trioxide deposit hardly took up oxygen at all, whereas the wall of the apparatus took up some amount of oxygen. It is evident that excited molecules and atoms of oxygen were produced by the discharge and a part of them were taken up by the wall. In the reaction of water vapor with tungsten, too, excited molecules and atoms of oxygen would be produced and a part of them be taken up by the wall by chemisorption. Langmuir[9] has found that oxygen adsorbed on tungsten evaporates from the surface as atoms when the surface is nearly bare. Therefore, it is most reasonable to consider that the ratio value greater than 3 is caused by the fact that some amount of hydrogen is liberated, not being accompanied by the weight loss of filament, since oxygen is produced by the decomposition of water vapor and is taken up by the wall of the apparatus, and to consider that the reaction rate and the ratio value O/W of deposit decrease with the increase of hydrogen pressure, since oxygen thus taken up reacts with hydrogen to form water vapor.

Summary

1) Reaction probabilities above 1950°K are determined.

2) The ratio value O/W of the deposit increases with the rise of temperature.

3) The deposit having ratio value O/W greater than 3 appears colorless in transmitted light.

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4) The colorless deposit is composed of tungsten trioxide and the ratio value O/W greater than 3 is ascribed to the production of hydrogen, not being accompanied by the weight loss of filament, since the ratio value is determined from the amount of hydrogen produced and the amount of weight loss of filament.

5) Water vapor decomposes and a part of the oxygen thus produced is taken up by the wall of the apparatus, and hence hydrogen is produced, not being accompanied by the weight loss of filament.

6) The reaction rate and the ratio value O/W of the deposit decrease with the increase of hydrogen pressure, since the oxygen taken up by the wall recombines with hydrogen to form water vapor.

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Investigation on Mixed Complexes. III[1]*. Spectrophotometric Studies on Platinum(II) Complexes*

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In general, mixed complexes are easily formed, but it appears that mixed cyano complexes are not easily formed. For instance, many species of mixed ammine complexes of cobalt(III) and platinum(II) are known, but mixed cyano complexes of cobalt(III) and platinum(II) known hitherto are few[2], and they have a strong tendency to become cyano complexes[3].

In the preceeding paper[1] of this series, it was demonstrated that no mixed cyano complexes are formed in the case of nickel(II) and copper(I). However, these are the cases where the parent complexes (for instance, $[Ni\,en_3]^{2+}$ and $[Ni(CN)_4]^{2-}$) have different configuration from each other. In this article an experiment has been carried out on platinum(II) complexes, which have the same configuration, in order to verify whether the mixed cyano complex is formed or not.

Results and Discussion

It has been known that chloride ions in tetrachloro platinate(II) ion are replaced by cyanide ions in solution at room temperature. Though no mixed cyano complex of platinum(II) has ever been known, a possibility of its formation in solution is still in question. The experiment was undertaken to solve this problem.

A potassium cyanide solution was added to a solution of potassium tetrachloro platinate(II) in the ratios as indicated in Table I, and extinction measurements were carried out on each of the mixed solutions. The results are shown in Fig. 1.

The extinction curves in Fig. 1 show that only the tetracyano platinate(II) and tetrachloro platinate(II) ions are present, no mixed complex ions such as $[Pt\,Cl_3CN]^{2-}$, $[Pt\,Cl_2(CN)_2]^{2-}$ and $[Pt(CN)_3Cl]^{2-}$ being present; if any of the mixed complexes were formed, the absorption curve would be subject to deformation to some degree, or a new absorption maximum would appear correspondingly, in the region where tetracyano platinate(II) ion has no absorption.

TABLE I. THE COMPOSITION OF THE SOLUTIONS (cf. Fig. 1)

Solution number	(1)	(2)	(3)	(4)	(5)
0.03 F $K_2[Pt\,Cl_4]$ and 3 F KCl*	8 ml.	8	8	8	8
0.1220 F KCN	0 ml.	2	4	6	8
Water	8 ml.	6	4	2	0

* KCl is added to supress hydrolysis of $[Pt.Cl_4]^{2-}$.

1) Part II of this series: S. Kida, This Bulletin, 32, 981 (1959).

2) J. C. Bailar, "The Chemistry of the Coordination Compounds", Reinhold Publ. Co., New York (1956), p. 87, "General Survey".

3) This tendency can be seen when one compares the methods of preparation of the two complxes, $[Co(NH_3)_5Cl]^{2+}$ and $[Co(CN)_5Cl]^{3-}$; the pentammine complex is readily prepared from cobaltous salt, ammonia and ammonium chloride in an aqueous solution, while the pentacyano complex is obtained only by substitution of the cyanide ion for ammonia of petammine complex under a very delicate condition.

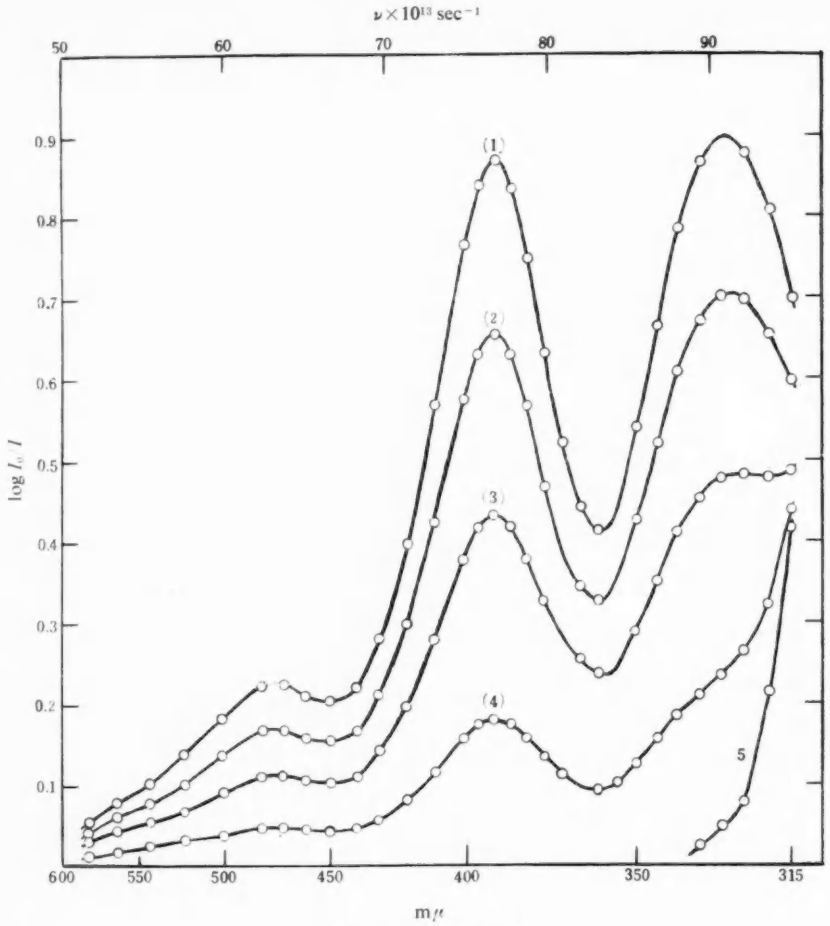

Fig. 1. (cf. Table I).

If it is assumed that all of the added cyanide ions are consumed to form the tetracyano platinate(II) ion, the calculated value of ([Pt] $-1/4[CN]$)/[Pt] must accord with the experimentally obtainable value, D/D_1[4], where [Pt] and [CN] denote the total concentration of all platinum species and of the added cyanide ion in each solution shown in Table I and Fig. 1. Actually, a satisfactory agreement between the calculated and the experimental value can be found in Table II.

A potassium cyanide solution was added to a solution of potassium tetrabromo platinate(II), in order to examine the substitution of the cyanide ion for the coordinated bromide. The result was the same in the case of the potassium tetrachloro platinate(II); i.e. the absorption curves are not deformed in the region where the tetracyano platinate(II) ion has no absorption, and the calculated value, ([Pt] $-1/4[CN]$)/[Pt] accords with the experimental value, D/D_0, as is shown in Fig. 2 and Table IV.

TABLE II

	(1)	(2)	(3)	(4)	(5)
([Pt] $-1/4[CN]$)/[Pt]	1.00	0.746	0.492	0.237	0
D/D_1 for 470 mμ	1.00	0.748	0.496	0.207	0
for 400 mμ	1.00	0.751	0.492	0.208	0
for 390 mμ	1.00	0.753	0.499	0.209	0
for 380 mμ	1.00	0.759	0.505	0.212	0

Numbers in the first row denote solution numbers in Table I.

4) If the reaction, $[PtCl_4]^{2-}+4CN^- \rightarrow [Pt(CN)_4]^{2-}+4Cl^-$, takes place quantitatively, optical densities of the solutions are expressed as in the following:
$D=\varepsilon_1([Pt]-1/4[CN])+\varepsilon_2(1/4[CN])$, and for solution 1, $D_1=\varepsilon_1[Pt]$, where ε_1 and ε_2 are extinction coefficients of $[PtCl_4]^{2-}$ and $[Pt(CN)_4]^{2-}$, respectively. However, in the region of 330~600 mμ the ratio D/D_1 can be reduced to ([Pt] $-1/4[CN]$)/[Pt], since in this region $\varepsilon_2=0$.

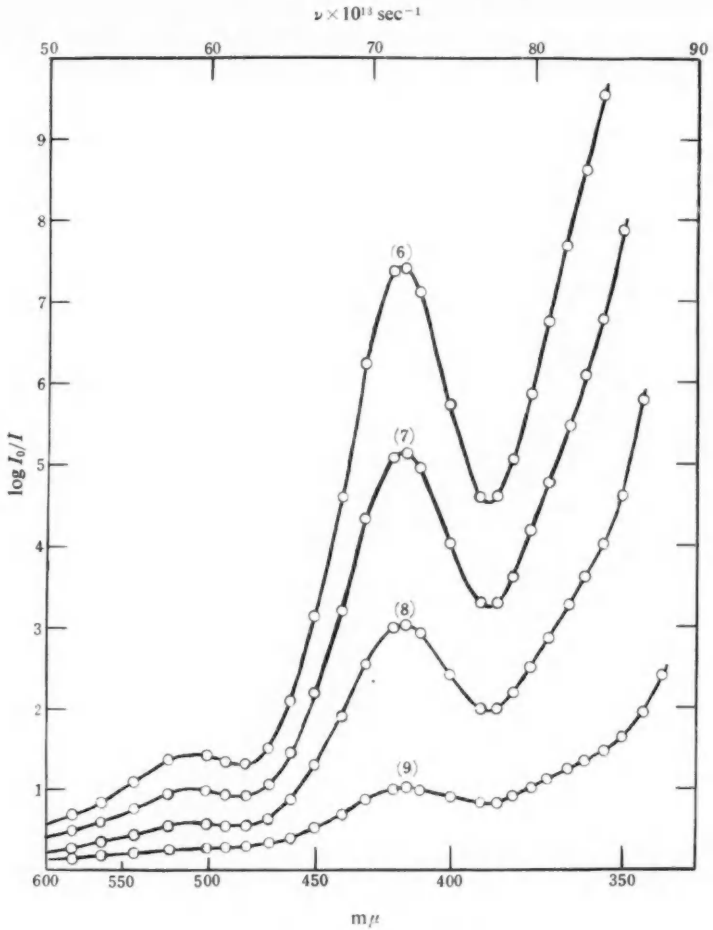

Fig. 2. (cf. Table III).

TABLE III. THE COMPOSITION OF THE SOLUTIONS (cf. Fig. 2)

Solution number	(6)	(7)	(8)	(9)	(10)
0.015 F $K_2[Pt\,Br_4]$ and 1 F KBr**	8 ml.	8	8	8	8
0.0703 F KCN	0 ml.	2	4	6	8
Water	8 ml.	6	4	2	0

** KBr is added to supress hydrolysis of $[Pt\,Br_4]^{2-}$.

TABLE IV

	(6)	(7)	(8)	(9)	(10)
$([Pt]-1/4[CN])/[Pt]$	1.00	0.707	0.414	0.121	0
D/D_6 for 520 mμ	1.00	0.691	0.403	0.187	0
for 420 mμ	1.00	0.690	0.407	0.137	0
for 410 mμ	1.00	0.697	0.411	0.140	0

Numbers in the first row denote solution numbers in Table III.

These results are the first example which evidently shows that no mixed complex is formed between the complexes of the same configuration. The cause of this phenomenon will be discussed in the last paper of this series[5].

Further experiments on the other compounds, especially on cobaltic complexes, to find further similar examples, are desirable. Unfortunately, however, it has been found difficult to find appropriate compounds to be examined for the present purpose.

When a potassium cyanide solution is added to a solution of hexammine cobalt(III) chloride, the coordinated ammonia is replaced by the cyanide ion, and the only product obtained is not easily soluble crystals, $[Co(NH_3)_6]\cdot[Co(CN)_6]$. From the above fact alone, one

5) S. Kida, to be published.

can not deduce a conclusion, because there are two probable cases; i.e. 1) the mixed complex is not formed because of its comparatively less stability, 2) although the mixed complexes are easily formed in solution, the least soluble compound, $[Co(NH_3)_6] \cdot [Co(CN)_6]$, separates out, and the equilibrium shifts to produce the crystals, $[Co(NH_3)_6] \cdot [Co(CN)_6]$.

Experimental

Extinction measurements were made by the Beckman DU Spectrophotometer using 1 cm. qualtz cells at room temperature.

Potassium tetrachloro platinate(II), $K_2[PtCl_4]$, and potassium tetrabromo platinate(II), $K_2[PtBr_4] \cdot 2H_2O$, were prepared according to the literatures[6,7], and their purity was checked by analyzing their quantity of halogen. The concentration of potassium cyanide was determined by a titration with a standard solution of silver nitrate.

6) W. C. Fernelius, "Inorganic Syntheses", Vol. II, McGraw- Hill Book Co., Inc., New York (1954), p. 87.
7) E. Billmann and A. C. Anderson, *Ber.*, **36**, 1566 (1903).

Summary

The spectrophotometric investigation has shown that in the substitution reactions of cyanide ion for halogens(X^-) of the complexes, $[PtX_4]^{2-}$, (X=Cl and Br) in solution, no mixed complex is formed.

The author wishes to thank Professor R. Tsuchida of Osaka University for his kind guidance throughout this work. He is also indebted to Dr. H. Yoneda and Dr. J. Fujita for their helpful discussions.

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Adsorption of the Ferric Ion by Weakly Acidic Resins. Preferential Uptake of the Ferric Ion by Alginic Acid

By Manabu SENŌ and Takeo YAMABE

(Received October 6, 1959)

Weakly acidic ion-exchange resins have strong affinity to the hydrogen ion and it is scarcely exchanged at all for other cations including heavy metal ions. Recently, it has been revealed[1,2] in the course of separation experiments of heavy metal ions that alginic acid adsorbs the ferric ion to a great extent, although it is a weakly dissociated acid.

In this paper, adsorptive properties for ferric ions of weakly acidic ion-exchange resins, Amberlite IRC-50 and alginate resin, are examined and discussed.

Experimental

The exchange resins used are Amberlite IRC-50 (Rohm and Haas Co., Ltd., U.S.A.) and alginic acid*. They were washed thoroughly with pure water and air-dried, after conditioning with acid and alkali.

All the equilibrium experiments were carried out by the batch-method. Resins of acidic form were used unless otherwise stated. About 0.2 g. of the resin and 50 ml. of the external salt solution were taken in a beaker and allowed to stand for a week or more with stirring occasionally, since the rate of exchange is rather low for weakly dissociated resins as shown by the preliminary test (Fig. 1). To prevent the vaporization of the solution, the beaker was covered with polyvinylchloride sheet. The concentrations of metal ions in the added solutions were about 0.03 meq./ml. except these described otherwise. After equilibrating, the metal and hydrogen ions remaining in solution were assayed and the amount of the metal ions adsorbed on the resin was estimated as usual. The iron, aluminum and copper were analyzed colorimetrically.

All reagents are of commercial special-grade and were used without further purification.

Absorption spectra were measured using a Hitachi EPU-2A spectrophotometer.

Results and Discussion

Exchange of the Hydrogen Ion for the Ferric Ion.—Quantitative data on the adsorption of the ferric ion by weakly acidic resins from chloride solutions of varying initial concentrations of

1) H. Specker and H. Hartkamp, *Z. anal. Chem.*, **140**, 167; **141** 33 (1953).
2) T. Takahashi and S. Emura, *Japan Analyst* (*Bunseki Kagaku*), **7**, 568 (1958).
* It was prepared by treating commerical sodium alginate (Kimitsu Chemical Industry, Co., Ltd.) with 10% hydrochloric acid, after it was once dissolved in water and filtered.

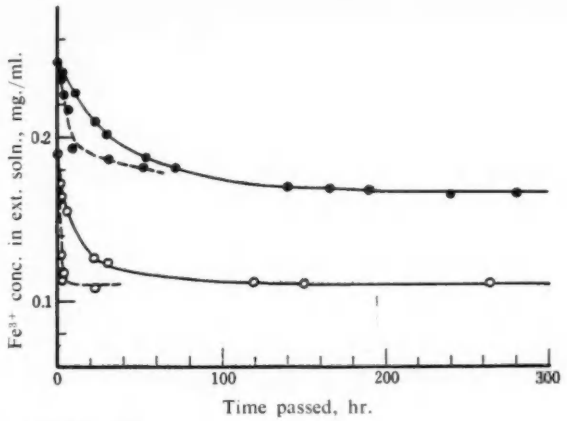


Fig. 1. Rate of exchange
○ Alginate resin, —— in settling
● Amberlite IRC-50, ---- with stirring
Resin, acidic form. Alg. 0.32 g., IRC-50 0.49 g.; Soln., 0.001 N HCl, 150 ml.

TABLE I. EXCHANGE OF THE HYDROGEN ION FOR THE FERRIC ION

	Fe^{3+} exchanged, meq./g. resin (eq./eq. resin)			
HCl concn., N	0	0.001	0.01	0.1
Amberlite IRC-50	4.57(0.44)	2.53(0.24)	1.06(0.10)	0.93(0.09)
Alginate resin	6.67(1.17)	3.88(0.68)	3.54(0.62)	2.12(0.37)
Amberlite IR-120	5.90(1.26)	5.54(1.18)	5.13(1.09)	3.42(0.73)

Resins, acid form 0.1~0.2 g.
Ferric chloride soln., 0.5 mg. Fe^{3+}/ml., 50 ml.

TABLE II. AMOUNTS OF IONS REMAINING IN SOLUTION PHASE BEFORE AND AFTER EQUILIBRIUM

	Amounts, meq./ml.					
	Orig. ext. soln.			Equil. ext. soln.		
	H^+	Fe^{3+}	Cl^-	H^+	Fe^{3+}	Cl^-
Alginate resin (0.21 g.)	0.0010	0	0.0012	0.0011	0	0.0012
	0.0010	0.0141	0.0152	0.0059	0.0082	0.0153
	0.0010	0.0282	0.0302	0.0056	0.0223	0.0303
Amberlite IRC-50 (0.16 g.)	0.0010	0	0.0012	0.0011	0	0.0012
	0.0010	0.0141	0.0152	0.0019	0.0135	0.0152
	0.0010	0.0282	0.0302	0.0042	0.0250	0.0298

hydrochloric acid were given in Table I. Alginate resin adsorbs the ferric ion more strongly than Amberlite IRC-50. Amounts of ferric ions adsorbed were markedly dependent on pH of the external solution. For comparison, the data on exchange by a strongly acidic ion-exchange resin, Amberlite IR-120, were also shown in the table.

It is interesting to note that the adsorption capacity for the ferric ion is larger than the total exchange capacity**, which is obtained

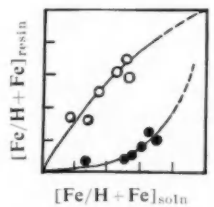


Fig. 2. Exchange diagram between hydrogen and ferric ions.
○ Alginate resin
● Amberlite IRC-50

** The total exchange capacities are 10 for Amberlite IRC-50, 5.6 for alginate and 4.5 (meq./g. resin) for Amberlite IR-120, respectively.

from a titration curve by alkali, in the case of alginic acid and Amberlite IR-120.

In Fig. 2, the equilibrium diagram of the ferric ion against the hydrogen ion was shown. It is noteworthy that the ferric ion is adsorbed by alginate resin to almost the same extent as the hydrogen ion.

In Table II, the amounts of all ions remaining in external solution before and after equilibrium of the exchange reaction were described. As seen in the table, the adsorption of the ferric ion is intrinsically an exchange reaction of counter-ions of the resins.

Preferential Adsorption of the Ferric Ion.—In Table III and Fig. 3, the results of exchange equilibria of other heavy metal ions, Fe^{2+}, Al^{3+} and Cu^{2+}, for the hydrogen ion were given. As shown already by other investigators[1], who tried successfully to separate the ferric ion from other metal ions by columns of alginic acid powder, alginate resin combines very strongly with the ferric ion compared with other heavy metal ions. This behavior is a remarkable character of alginate resin, in contrast with Amberlite IR-120 and IR C-50; the former adsorbs well all metal ions and the latter has a very strong affinity to the hydrogen ion and, therefore, metal cations replace the hydrogen ion with difficulty.

This result is valid, independently of the acidity of the external solution as seen in Table IV. Of course, as the acidity of a solution becomes very high, these resins can not combine with other cations except in the case of the hydrogen ion.

To confirm this selective uptake of the ferric ion by alginic acid, the exchange equilibria between Fe^{3+} and Al^{3+} or Cu^{2+} were examined under the condition that the concentration of hydrochloric acid in salt solution was kept constant. Also the total concentration of the metal ions in the system was almost kept constant, 0.15 meq./ml. The results were given in Fig. 4. Preferential adsorption of the ferric

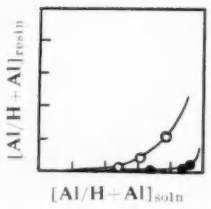


Fig. 3. Exchange diagram between hydrogen and aluminum ions.
○ Alginate resin
● Amberlite IRC-50

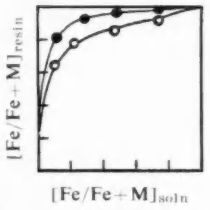


Fig. 4. Exchange equilibria of alginate resin between Fe^{3+} and Al^{3+} or Cu^{2+} at a constant acid concentration, 0.01 N H_2SO_4.
○ Fe^{3+}~Cu^{2+}, ● Fe^{3+}~Al^{3+}

TABLE III. EXCHANGE OF THE HYDROGEN ION FOR HEAVY METAL IONS IN SOLUTION OF CONSTANT ACID CONCENTRATION, 0.01 N

	Ions exchanged, meq./g. resin			
Ions	Fe^{3+}	Fe^{2+}	Al^{3+}	Cu^{2+}
Salt form	$FeCl_3$	$FeCl_2$	$Al_2(SO_4)_3$	$CuSO_4$
Amberlite IRC-50	1.06	0	0.20	0
Alginate resin	3.54	0.13	0.50	1.17
Amberlite IR-120	5.13	4.02	4.84	4.36

Resins, acid form 0.1~0.2 g.
Metal ion soln., ca. 0.03 meq./ml., 50 ml.

TABLE IV. EXCHANGE OF THE HYDROGEN ION FOR THE FERROUS OR THE ALUMINUM ION

	Ions exchanged, meq./g. resin			
Fe^{2+}, $FeCl_2$-HCl (0.60 mg. Fe^{2+}/ml., 50 ml.)				
HCl concn., N	0	0.001	0.01	0.1
Amberlite IRC-50	0.12	0.05	0	0
Alginate resin	0.41	0.23	0.13	0.05
Al^{3+}, $Al_2(SO_4)_3$-H_2SO_4 (0.25 mg. Al^{3+}/ml., 50 ml.)				
H_2SO_4 concn. N	0	0.0001	0.001	0.01
Amberlite IRC-50	0.28	0.22	0.19	0.17
Alginate resin	2.18	2.06	1.49	0.47

Resin, acid form 0.1~0.2 g.

Table V. Desorption of metal ions with acid from resins

Added soln.		Ions retained, meq./g. resin			
		H_2O	0.01 N HCl	0.1 N HCl	1.0 N HCl
Alginate resin	Fe^{3+}	6.98	6.06	1.44	0
	Al^{3+}	4.33	2.75	0.53	0
	Cu^{2+}	4.61	3.18	0.11	0
Amberlite IRC-50	Fe^{3+}	6.00	4.97	0.02	0
	Al^{3+}	5.93	3.78	0.43	0
	Cu^{2+}	6.33	4.00	0	0

Resin, metal salt form 0.3~0.4 g., soln., 100 ml.

Table VI. Effect of anion on adsorption of the ferric ion

Salt form	Fe^{3+} adsorbed, meq./g. resin			
	$FeCl_3$	$Fe(NO_3)_3$	$Fe_2(SO_4)_3$	$FeK(SO_4)_2$
HCl concn., N	0.0135_6	0.0100_5	0.0110	0.0111
Amberlite IRC-50	1.07	1.07	0.98	1.05
Alginate resin	3.24	2.96	3.14	3.09

Resin, acid form 0.1~0.2 g.
Ferric ion soln., 0.5 mg./ml., 50 ml.

ion against the aluminum or copper ion is very remarkable and, therefore, it is clear that the ferric ion can easily be separated from these ions by using alginic acid as an ion-exchange resin.

Desorption of Metal Ions from Resins with Acid.—Although in all the experiments mentioned above the acidic form resins were equilibrated with salt solution, here salt form resins were treated with acid to examine the reversibility of these exchange reactions. Resin of Fe^{3+}-, Al^{3+}- or Cu^{2+}- salt form was prepared by treating sodium salt form resin with ferric, aluminum or cupric chloride solution respectively, and washing it several times with pure water.

A definite quantity of each salt resin was immersed in an acid solution of known concentration, and the amount of metal ion desorbed from resin was measured. The results were given in Table V.

The reversibility of the exchange equilibrium does not always hold. It must be pointed out that, in the case of Amberlite IRC-50, the amounts of metal ions retained in this elution experiment are larger than those adsorbed in the adsorption experiment, independently of the variety of ion species. Alginate resin adsorbs ferric ion remarkably and the retained quantity is nearly equal to the adsorbed one shown in Table I.

Metal ions are eluted from resins almost with 0.1 N and completely with 1 N hydrochloric acid.

Effect of Anion.—The effect of anion on adsorption of the ferric ion by resin was examined and the result was given in Table VI.

In both resins the effect of anion is not remarkable.

Mechanism of Ferric Ion Adsorption on Resins.—As mentioned above, alginic acid resin adsorbs the ferric ion more extensively than Amberlite IRC-50 and the ferric ion is more preferentially adsorbed than other heavy metal ions, aluminum and copper ions, by these weakly dissociated resins. Taking into account these facts and the structural character of resins, the mechanism of adsorption of the ferric ion on these resins is examined as follows:

Adsorption of Chloride Complex Ions, $FeCl_n^{+(3-n)}$.—It is well-known[3,4] that the ferric ion combines with the chloride ion to form complex ions, $FeCl_n^{+(3-n)}$, where n becomes four at higher chloride concentration. If these complex ions take a part in the exchange reaction, adsorption of the chloride ion must be observed. However, this is not the case as shown in Table II, probably because the chloride concentration is rather low, less than 0.1 N, and the formation of chloride complexes is not predominant.

Adsorption of Hydroxy Complex Ions, $Fe(OH)_n^{+(3-n)}$.—Since in this experimental condition the hydrogen ion concentration is low in external medium, the ferric ion is hydrolyzed partially and the hydroxy complex ions, $Fe(OH)^{+2}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3$, may be formed to a large extent[3,5]. Moreover, the fact that the exchanged quantity of the ferric ion is greater than the total exchange capacity leads to the conclusion that the ferric ion is exchanged not as a trivalent cation but as an ion with less valency on the average.

3) E. Rabinowitch and W. H. Stockmayer, *J. Am. Chem. Soc.*, **64**, 335 (1942).
4) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, **1953**, 1435.
5) A. B. Lamb and A. G. Jacques, *J. Am. Chem. Soc.*, **60**, 967, 1215 (1938).

For these reasons, it seems to be a fact that these hydroxy complexes have a part in the exchange reaction. None of the present experiments oppose the above deduction. It supports the probability of this adsorption mechanism that, when alginic acid combines with the ferric ion, it colors to reddish-brown and has a very similar absorption spectrum to that of the ferric hydroxide sol and of $Fe(OH)^{2+}$ given by Rabinowitch et al. (Fig. 5)[3].

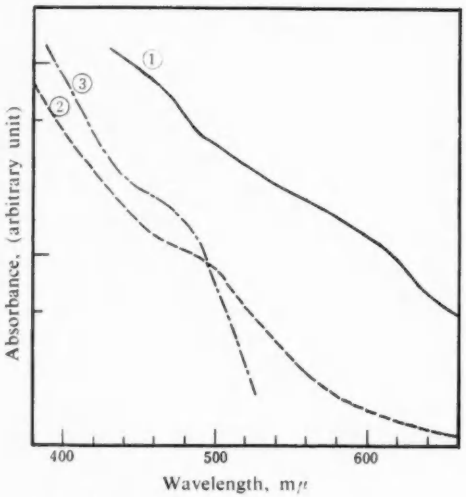


Fig. 5. Absorption spectra of
1. alginate resin membrane adsorbing ferric ion against original alginate membrane,
2. ferric hydroxide sol and
3. $Fe(OH)^{2+}$ given by Rabinowitch et al.[3]

In a case when partially hydrolyzed ions, e.g. $Fe(OH)^{2+}$, play a part in the adsorption reaction, reactions of various types may proceed at the same time. For instance, besides the normal exchange reaction 1

$$2HAlg + Fe(OH)^{2+} \rightleftarrows Fe(OH)Alg_2 + 2H^+ \quad (1)$$

the following reactions including neutralization may occur

$$HAlg + Fe(OH)^{2+} \rightleftarrows Fe(Alg)^{2+} + H_2O$$

$$Fe(Alg)^{2+} + 2HAlg \rightleftarrows Fe(Alg)_3 + 2H^+$$

that is,

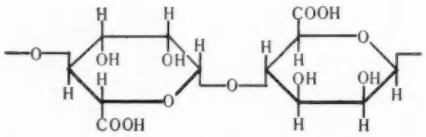
$$3HAlg + Fe(OH)^{2+} \rightleftarrows Fe(Alg)_3 + 2H^+ + H_2O \quad (2)$$

where Alg denotes a structural unit of alginate resin. Taking the hydrolysis of ferric alginate into account, reactions 1 and 2 cause the same result.

Although the present study can not give any confirmative evidence for the occurrence of these reactions, it is probably true that this mechanism may play an important part in the adsorption of the ferric ion by weakly acidic resin, for neutralization reaction can proceed to a large extent in these weakly dissociated resins.

The detailed discussion of such an exchange reaction including reactions of various types must be made clear in future.

Complex Adsorption.—As alginic acid has the following structure containing two hydroxyl groups and an oxygen linkage, it may be expected to combine with the ferric ion, forming an inner salt complex. To examine the effect



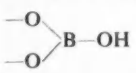
of the hydroxyl groups on the adsorption of the ferric ion by alginic acid, the ferric ion adsorbed on alginate resin was estimated when boric acid was added to the equilibrating system. The result was given in Table VII. The addition

TABLE VII. ADSORPTION OF THE FERRIC ION BY ALGINATE RESIN IN THE PRESENCE OF BORIC ACID

HCl concn., N	0	0.001	0.01	0.1
Fe^{3+} adsorbed, meq./g.	3.28	2.84	2.04	1.99

Boric acid, 1.0 meq. (equiv. to alginate)
Alginate resin, 0.2 g.
Ferric chloride soln., 0.5 mg. Fe^{3+}/ml., 50 ml.

of boric acid diminishes the adsorbed quantity of ferric ions. Since it is known[6] that alginic acid having a *cis*-diol group combines with boric acid to form a chelate compound,



it is confirmed that the presence of the hydroxyl groups influences the adsorption of the ferric ion.

Moreover, to obtain further knowledge concerning the formation of a chelate compound between alginic acid and the ferric ion, absorption spectra of the ferric ion were measured in the presence of glucuronic acid, which is similar structurally to the unit of alginic acid***. As

6) H. Deuel and M. Neukom, *Makromol. Chem.*, **3**, 13 (1949).

*** The structural unit of alginic acid is mannuronic acid and glucuronic acid may be structurally named galacturonic acid. However, it is safely considered that qualitative behaviors toward the ferric ion are similar for both acids.

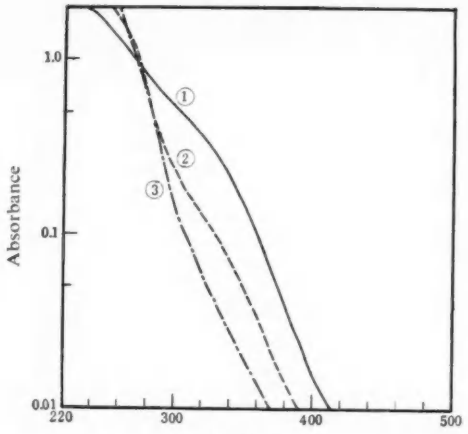


Fig. 6. Absorption spectra of ferric perchlorate $Fe(ClO_4)_3$, 0.0022 meq./ml.; $HClO_4$, 1, 0.007 N; 2, 0.031 N; 3, 0.091 N. Reference, H_2O.

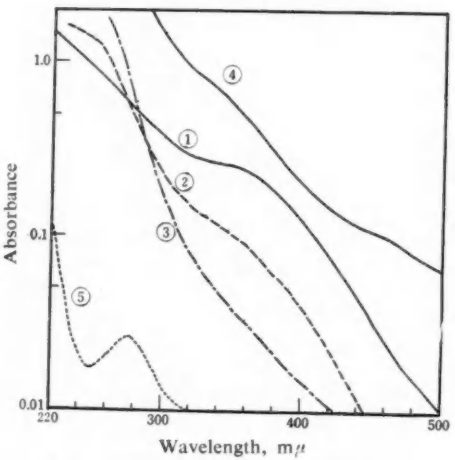


Fig. 7. Absorption spectra of Fe^{3+}~glucuronate.

	$Fe(ClO_4)_3$	$HClO_4$	Na glu.
1	0.0022	0.007	0.0022 meq./ml.
2	〃	0.031	〃
3	〃	0.091	〃
4	〃	0.007	0.022
5	0	0	0.0022

reference, H_2O.

shown in Figs. 6 and 7, it is apparent that there is a shoulder at 320~340 mμ region of the absorption spectrum of the ferric ion in the presence of the glucuronate ion. That is to say, an absorption band appears at about 330 mμ and becomes weaker as the acidity of the solution increases and disappears at 0.1 N of perchloric acid.

When the concentration of the glucuronate ion is high, a weak absorption is observed over the visible wavelength region and the solution becomes weakly reddish-yellow. The absorption at 330 mμ does not become remarkable and a new weak band appears at 470 mμ.

The visible absorption spectrum**** of alginate membrane adsorbing the ferric ion also has a shoulder at 460~470 mμ, as shown in Fig. 5.

The component ions, ferric (aquo), glucuronate and alginate ions, exhibit no absorption peak in these regions[7]. Therefore, although these spectroscopic characters can not be explained completely in the present stage, it may be concluded that there are some interactions between the ferric ion and the glucuronate or alginate ion besides the simple coulombic one. Thus, it is, partly at least, due to the complex formation that alginate resin adsorbes the ferric ion intensively and preferentially.

It must be noticed that a hydroxy complex of the ferric ion has an absorption spectrum over the visible wavelength region and this spectrum has a shoulder at 460~480 mμ, as revealed from the spectrum of the ferric hydroxide sol and the spectrum of $Fe(OH)^{2+}$ obtained by Rabinowitch et al.[3] Since the concentration of the hydrogen ion is higher in the resin phase than in the external solution, it can not be expected that these hydroxy complexes exist in a free state, but it may be probable that hydroxy complexes are formed between the ferric ion and the glucuronate or alginate ion.

The absorption spectra of the ferric ion in the presence of acetate and *p*-toluene sulfonate ions were shown in Figs. 8 and 9. These ions are structurally similar to a unit of Amberlite IRC-50 and Amberlite IR-120, respectively. The spectrum of the ferric ion is not affected by the addition of the former[8] and the addition of the latter does not change in shape, but shifts the spectrum of the ferric ion to a longer wavelength. From these observations it may be concluded that these ions do not combine with the ferric ion to form chelate compounds.

**** It was measured against the original alginate membrane using opal-glass. Measurements in the region of ultraviolet wavelengths are impossible by this method.

7) Ther is a peak at 270~280 mμ in the absorption spectrum of the glucuronate ion. The chloride complexes of the ferric ion have an absorpion peak at 330~340 mμ.

8) W. Reiss et al.[9] reported that ferric acetate complex exhibits absorption peaks at 337.5 and 465 mμ when the concentration of the acetate ion is high. These peaks were not detected under the present experimental condition.

9) W. Reiss, J. F. Hazel and W. M. McNabb, *Anal. Chem.*, **24**, 1647 (1952).

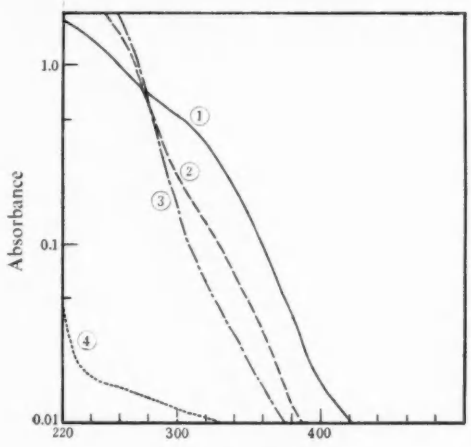


Fig. 8. Absorption spectra of Fe^{3+}~acetate.

	$Fe(ClO_4)_3$	$HClO_4$	Na acet.
1	0.0022	0.007	0.0022 meq./ml.
2	〃	0.031	〃
3	〃	0.091	〃
4	0	0	〃

reference, H_2O.

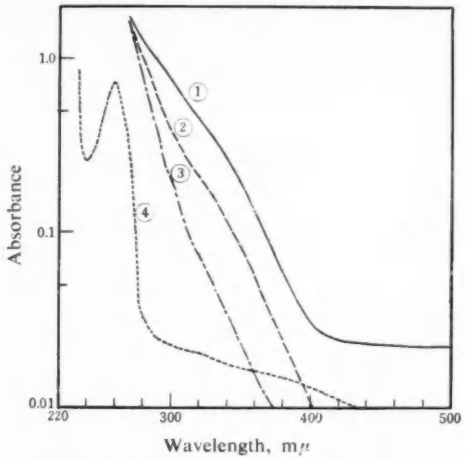


Fig. 9. Absorption spectra of Fe^{3+}~*p*-toluene sulfonate.

	$Fe(ClO_4)_3$	$HClO_4$	Na-*p*-TS.
1	0.0022	0.007	0.0022 meq./ml.
2	〃	0.031	〃
3	〃	0.091	〃
4	0	0	〃

reference, H_2O.

Summary

The exchange adsorptions of the ferric ion by the cation-exchange resins of carboxylic acid type, Amberlite IRC-50 and alginate resin, were examined. Equilibration experiments revealed that alginate resin adsorbs metal ions more extensively than Amberlite IRC-50 and the ferric ion is preferentially adsorbed by these resins, especially by alginate resin. The mechanism of adsorption of the ferric ion was discussed and it was concluded that the preferential uptake of the ferric ion by alginate resin was due to the partial hydrolysis of the ferric ion and the complex formation between the ferric ion and alginate resin.

In concluding this paper, the authors wish to express their thanks to Professor T. Takahashi for his continuous advice. The cost of the present research has been partly defrayed from the grant of the Ministry of Education, for which the authors' thanks are due.

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Studies on the Chemical Constitution of Agar-agar. XXII.[1] *Partial Methanolysis of Methylated Agarose of Gelidium Amansii*

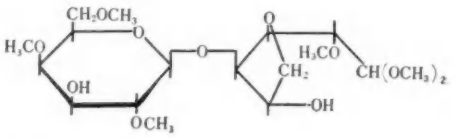
By Choji ARAKI and Susumu HIRASE

(Received October 8, 1959)

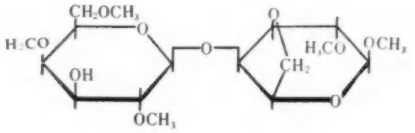
Agarose, a chief polysaccharide of agar, has been suggested by Araki[2], one of the present authors, to be a chain composed of alternating β-D-galactopyranose and 3,6-anhydro-α-L-galactopyranose residues. The preceding paper[1] concerned with the complete methanolysis of methylated agarose of *Gelidium amansii* provided a strong evidence to verify the above mentioned structure of agarose. A further support has now been obtained herein by partial methanolysis of the methylated polysaccharide.

The partial methanolysis was conducted with 0.5% methanolic hydrogen chloride for four hours, during which time 74% of the methylated polysaccharide was concerned in reaction. After treatment with barium hydroxide, the products were separated into neutral and acid components by fractionation with ether. The acidic component in the barium salt was obtained in too small a yield to be of structual significance. Further separation of the neutral components on a charcoal-Celite column led to the isolation of *O*-2, 4, 6-tri-*O*-methyl-β-D-galactopyranosyl-(1→4)-2-*O*-methyl-3, 6-anhydro-L-galactose dimethylacetal (I) and methyl *O*-2, 4, 6-tri-*O*-methyl-β-D-galactopyranosyl-(1→4)-2-*O*-methyl-3, 6-anhydro-β-L-galactopyranoside (II), both being derivatives of agarobiose (4-*O*-β-D-galactopyranosyl-3, 6-anhydro-L-galactose), which constitutes the repeating units of the agarose molecule. The total yield of compounds I and II amounted to 82% of the neutral products by weight.

The dimethylacetal (I) was eluted from the chromatographic column with 10～20% ethanol in water at 26～27°C and isolated in a crystalline form with the empirical formula $C_{12}H_{16}O_5\cdot(OCH_3)_6$. Further, methylation with methyl iodide and silver oxide afforded hexa-*O*-methylagarobiose dimethylacetal, which on methanolysis yielded methyl 2, 3, 4, 6-tetra-*O*-methyl-α, β-D-galactoside and 2, 5-di-*O*-methyl-3, 6-anhydro-L-galactose dimethylacetal, identifying thereby compound I as a derivative of agarobiose. Hydrolysis with 0.02 N oxalic acid solution removed two methoxyl groups from the molecule to yield tetra-*O*-methylagarobiose, indicating that the compound I was a dimethylacetal. On methanolysis the compound I produced a mixture of methyl 2, 4, 6-tri-*O*-methyl-α, β-D-galactosides, methyl 2-*O*-methyl-3, 6-anhydro-β-L-galactopyranoside and 2-*O*-methyl-3, 6-anhydro-L-galactose dimethylacetal, the separation of the mixture being effected by selective hydrolysis of the anhydrosugar derivatives followed by fractionation with *n*-hexane. This established the positions of the four methoxyl groups connected in ether linkages with the rest of the molecule of compound I.



(I)



(II)

The methyl glycoside (II) was eluted from the charcoal column with 50% ethanol in water at 26～27°C and isolated in a crystalline form with the empirical formula $C_{12}H_{15}O_5(OCH_3)_5$. When treated with boiling methanol containing 3% of hydrogen chloride, it was converted with ease into the fore-going dimethylacetal (I). Hydrolysis of compound II with 0.02 N oxalic acid solution resulted in the formation of the reducing sugar identical with that obtainable from the dimethylacetal (I). These facts have enabled to be assigned structure II to the compound under problem, the β-configuration of the glycosidic methoxyl group being suggested on the basis of the positive value of optical rotation. Moreover, further methylation of compound II with methyl iodide and silver oxide afforded crystalline methyl penta-*O*-methyl-β-agarobioside, which agreed in all respects

1) Part XXI: C. Araki and S. Hirase, This Bulletin, 33, 291 (1960).
2) C. Araki, This Bulletin, 29, 543 (1956); *Memoirs Fac. Ind. Arts, Kyoto Tech. Univ.*, 5, 21 (1956).

with the methylated disaccharide derivative previously isolated by Araki[3], one of the present authors, by re-methylation of the methanolysis products of methylated agarose of *G. amansii*.

The isolation of compounds I and II in a good total yield emphasizes that agarobiose units are repeated through their 1 and 3′ positions in the molecule of agarose of *G. amansii* as previously suggested by Araki.

Experimental

Evaporation and concentration of solutions were carried out under reduced pressure below 40°C. Melting points are uncorrected.

Methanolysis of Methylated Agarose.—Methylated agarose (10 g.) was suspended in methanol (150 ml.) containing 0.5% of hydrogen chloride and the suspension was heated under reflux for four hours, at which time undissolved material was removed by filtration. The filtrate was neutralized with silver carbonate, refiltered and evaporated to afford a sirup, which was then treated with 0.2 N barium hydroxide solution (100 ml.) at 60°C for two hours to saponify the methyl ester of the acidic component. The excess of the barium hydroxide was removed by neutralization with carbon dioxide and subsequent filtration, and the filtrate was evaporated to a sirup (7.4 g.).

Separation of Neutral and Acidic Components.—When the sirup obtained above was dissolved in ether (150 ml.), the acidic component was precipitated as a barium salt form. It was filtered off, washed with ether and dried in vacuo; yield, 0.18 g., $[\alpha]_D^{27}$ −26.4° in water (*c* 0.72). Evaporation of the filtrate afforded a mixture of neutral components as a colorless sirup; yield, 7.2 g., $[\alpha]_D^{27}$ −1.21° in water (*c* 0.83).

Chromatographic Separation of Mixture of Neutral Components.—The mixture of the neutral components (7.2 g.) obtained above was chromatographed at 25~27°C on a column (5.2×20 cm.) packed with charcoal (60 g.)and Celite (40 g.), successively higher concentrations of ethanol in water being used as developing solvents. The effluents were collected in separate receivers and evaporated to dryness to recover the contents, which were then weighed and the specific optical rotation, the methoxyl content and the molecular weight were measured. The results are shown in Table I.

TABLE I. CHROMATOGRAPHIC SEPARATION OF THE MIXTURE OF NEUTRAL COMPONENTS

Fraction	Developer %*	l.	Yield g.	$[\alpha]_D^{27}$ (°)H_2O	OCH_3 %	M.W.**
I	5	5	0.3	−0.6	42.1	211
II	7.5	5	0.5	+97.8	48.3	225
III	10	5	1.6	−29.3	43.3	423
IV	15	5	1.8	−30.8	43.1	423
V	20	5	0.8	−30.9	43.2	425
VI	30	6	0.4	−11.0	40.8	410
VII	50	3	1.1	+38.4	39.6	398
VIII	70	2	0.1	+39.0	39.5	395

* Concentration of ethanol in water.
** Molecular weight was determined by Rast's method.

Fractions I and II were obtained as colorless sirups, but on standing the latter fraction crystallized partly. Papar chromatographic examination, using cyclohexanol saturated with water as a mobile phase[1] and *O*-aminophenol in aqueous ethanol acidified with phosphoric acid as a spraying reagent[4], indicated the presence of 2-*O*-methyl-3,6-anhydro-L-galactose dimethylacetal (R_f 0.67) and methyl 2-*O*-methyl-3,6-anhydro-β-L-galactopyranoside (R_f 0.77) in fraction I and of the latter compound in fraction II. When these were hydrolyzed with 1 N sulfuric acid for five hours in a boiling water bath and subsequently examined on paper chromatograms with *n*-butanol-ethanol-water (4 : 1 : 2) as a mobile phase and aniline hydrogen phthalate in moist *n*-butanol as a spraying reagent, 2,4,6-tri-*O*-methyl-D-galactose was detected in the hydrolyzates of both fractions I and II, the anhydrosugar derivatives being decomposed during the hydrolysis. It was therefore considered that fraction I was a mixture of 2-*O*-methyl-3,6-anhydro-L-galactose dimethylacetal, methyl 2-*O*-methyl-3,6-anhydro-L-galactopyranoside and methyl 2,4,6-tri-*O*-methyl-D-galactoside and that fraction II was a mixture of the latter two.

On the other hand, fractions III—V were proved to be entirely the dimethylacetal (I), and fractions VII and VIII were also proved to be entirely the methyl glycoside (II) as described below. Fraction VI seemed to be a mixture of compounds I and II.

Tetra-*O*-methylagarobiose Dimethylacetal (I).—All fractions III—V in Table I crystallized completely on standing and melted at 84~86°C. These were combined and recrystallized twice from ether containing a small amount of petroleum ether, affording the dimethylacetal (I) in prisms; m. p. 88~89°C, $[\alpha]_D^{10}$ −25.2° in water (*c* 1.19), $[\alpha]_D^{10}$ −41.9° in methanol (*c* 1.05) and $[\alpha]_D^{10}$ −46.7° in chloroform (*c* 1.07). The crude yields of the dimethylacetal thus amounted to 58% of the sample applied.

Found: C, 50.65; H, 8.06; OCH_3, 43.45; mol. wt., 425. Calcd. for $C_{12}H_{16}O_5(OCH_3)_6$: C, 50.69; H, 8.04; OCH_3, 43.67%; mol. wt., 426.5.

Methanolysis of Dimethylacetal (I).—The dimethylacetal (I) (1.5 g.) obtained above was dissolved in 3% methanolic hydrogen chloride (30 ml.) and heated under reflux for two hours, at which time the optical rotation of the solution reached a constant value ($[\alpha]_D$ −29° → +42°). The solution was neutralized with silver carbonate, filtered and evaporated to dryness, when a mixture of methyl 2-*O*-methyl-3,6-anhydro-β-L-galactopyranoside, 2-*O*-methyl-3,6-anhydro-L-galactose dimethylacetal and methyl 2,4,6-tri-*O*-methyl-D-galactoside was obtained as a sirup (1.3 g.); $[\alpha]_D^{25}$ +51.0° in water (*c* 1.0).

a) Identification of methyl 2,4,6-tri-O-methyl-α,β-D-galactosides.—The sirup obtained above was

3) C. Araki, *J. Chem. Soc. Japan, (Nippon Kwagaku Kwaishi)*, **26**, 733 (1941).

4) S. Hirase, C. Araki and S. Nakanishi, This Bulletin **26**, 183 (1953).

5) S. M. Partridge, *Nature*, **164**, 443 (1949).

heated with 0.02 N oxalic acid solution for two hours in a boiling water bath to hydrolyze selectively the derivatives of 2-*O*-methyl-3,6-anhydro-L-galactose. The resulting product was isolated as a sirup in the usual manner and then extracted seven times each with 15 ml. of *n*-hexane at 50°C. The extracts were combined and evaporated to dryness, an anomeric mixture of methyl 2,4,6-tri-*O*-methyl-D-galactosides being obtained as crystals; yield, 0.50 g., m. p. 44~60°C, $[\alpha]_D^{27}$ +81.6° in water (*c*. 0.38), OCH_3 found: 51.67% (calcd. for $C_6H_5O_2(OCH_3)_4$: 52.52%). The methyl glycoside was identified by conversion in the usual manner into the corresponding reducing sugar[6], m. p. and mixed m. p. 109~110°C, $[\alpha]_D^{26}$ +116° → +90.1° in water (*c* 0.81), and its aniline derivative, m. p. and mixed m. p. 174°C, $[\alpha]_D^{26}$ −103° (initial) in acetone (*c* 0.40).

b) Identification of 2-O-methyl-3,6-anhydro-L-galactose.—The residual sirup, which had been separated from the methyl tri-*O*-methyl-D-galactoside by extraction with *n*-hexane as mentioned above was dissolved in acetone (5 ml.) and filtered. Evaporation of the filtrate afforded 2-*O*-methyl-3,6-anhydro-L-galactose[1] (0.65 g.), which seemed to be still contaminated with appreciable quantities of the methyl tri-*O*- methyl-D-galactoside as indicated by its positive value of the optical rotation $[\alpha]_D^{27}$ +24.1° in water (*c* 0.83) and its high methoxyl value 28.43% (calcd. for $C_6H_9O_4(OCH_3)$: 17.59%). But, without further purification, the sugar was oxidized with bromine water in the usual manner, and the resulting 2-*O*-methyl-3,6-anhydro-L-galactonic acid was crystallized from ethyl acetate; yield, 0.41 g., m. p. and mixed m. p. 141~142°, $[\alpha]_D^{25}$ −70.8° in water (*c* 0.72). One of the present authors has reported m. p. 142°C and $[\alpha]_D^{12}$ −70.0° in water for 2-*O*-methyl-3,6-anhydro-L-galactonic acid[7].

Hexa-*O*-methylagarobiose Dimethylacetal from I.—The dimethylacetal (I) (1.0 g.) was methylated twice with methyl iodide (15 g.) and silver oxide (10 g.) in the usual manner, giving hexa-*O*-methylagarobiose dimethylacetal as a colorless sirup; yield, 1.0 g., $[\alpha]_D^{10}$ −21.6° in water (*c* 1.11), $[\alpha]_D^{19}$ −37.3° in methanol (*c* 1.10), $[\alpha]_D^{19}$ −40.5° in chloroform (*c* 1.11), n_D^{25} 1.4611, OCH_3 found: 54.18% (calcd. for $C_{12}H_{16}O_5(OCH_3)_6$: 54.61%). One of the present authors has reported $[\alpha]_D^{23}$ −11.09° in water, $[\alpha]_D^{23}$ −29.46° in chloroform and n_D^{25} 1.4632 for hexa-*O*-methylagarobiose dimethylacetal[8].

Methanolysis of Hexa-*O*-methylagarobiose Dimethylacetal.—Hexa-*O*-methylagarobiose dimethylacetal (0.80 g.) obtained above was subjected to methanolysis with 3% methanolic hydrogen chloride (20 ml.) for twenty five hours. The hydrogen chloride was removed by neutralization with silver carbonate and filtration, and the filtrate on evaporation afforded a mixture of methyl 2,3,4,6-tetra-*O*-methyl-α, β-D-galactosides and 2,5-di-*O*-methyl-3,6-anhydro-L-galactose dimethylacetal; yield, 0.85 g., $[\alpha]_D^{10}$ +48.0° in water (*c* 1.00).

The mixture was separated at 10~13°C on a column (3.7×11 cm.) packed with charcoal and Celite into four fractions shown in Table II. Fraction I was identified as 2,5-di-*O*-methyl-3,6-anhydro-L-galactose dimethylacetal and fractions III and IV were done as methyl 2,3,4,6-tetra-*O*-methyl-α, β-D-galactosides as described below; while, fraction II seemed to be a mixture of the two components.

Table II. Separation of the products of methanolysis of hexa-*O*-methylagarobiose dimethylacetal

Fraction	Developer %*	l.	Yield g.	$[\alpha]_D^{13}$ (°)H_2O	n_D^{25}	OCH_3 %
I	7.5	2.0	0.20	− 30.9	1.4547	52.31
II	10	2.0	0.18	+ 36.0	1.4531	55.41
III	10	2.5	0.12	+180.0	1.4489	61.88
IV	12.5	2.0	0.06	+180.0	1.4488	61.85

* Concentration of ethanol in water.

a) Identification of 2,5-O-methyl-3,6-anhydro-L-galactose Dimethylacetal.—The properties of fraction I in Table II agree with those of 2,5-di-*O*-methyl-3,6-anhydro-L-galactose dimethylacetal, which have been recorded by the present authors as: $[\alpha]_D^{17}$ −6.90°[8] or $[\alpha]_D^{19}$ −6.67°[9] in water and n_D^{25} 1.4533[8] or n_D^{20} 1.4563[9].

For confirmative identification, the dimethylacetal (0.15 g.) was converted into 2,5-di-*O*-methyl-3,6-anhydro-L-galactonic acid by hydrolyzing with 3% hydrobromic acid for five minutes in a boiling water bath and then oxidizing with bromine in the usual manner. The resulting carboxylic acid (0.16 g.) was purified by recrystallization from ethyl acetate; m. p. and mixed m. p. 160~161°C, $[\alpha]_D^{12}$ −62.2° in water (*c* 0.90). The present authors[3,9] have reported m. p. 161°C, $[\alpha]_D^{23}$ −54.32° in water and $[\alpha]_D^{21}$ −61.9° in water for the compound.

Found: C, 46.45; H, 6.88; OCH_3, 30.38. Calcd. for $C_6H_5O_4(OCH_3)_2$: C, 46.60; H, 6.84; OCH_3, 30.12%.

b) Identification of Methyl 2,3,4,6-tetra-O-methyl-D-galactoside.—Fractions III and IV in Table II agree in properties with methyl 2,3,4,6-tetra-*O*-methyl-D-galactoside. The fractions were combined and hydrolyzed with 1 N sulfuric acid in the usual manner to give the corresponding reducing sugar, which was crystallized from *n*-hexane; m. p. and mixed m. p. 70~72°C, $[\alpha]_D^{12}$ +144.4° (initial) → +120° (final) in water (*c* 0.45).

Found: C, 50.41; H, 8.51; OCH_3, 52.45. Calcd. for $C_6H_5O_2(OCH_3)_4$: C, 50.83; H, 8.53; OCH_3, 52.52%.

Methyl Tetra-*O*-methyl-β-agarobioside (II).—Fractions VII and VIII in Table I crystallized completely and melted at 143~144°C. These were combined and recrystallized twice from ethyl acetate, affording the pure sample of compound II in prisms; m. p. 143~144°C, $[\alpha]_D^{10}$ +41.7° in water (*c* 1.15), $[\alpha]_D^{15}$ +23.6° in methanol (*c* 1.10) and $[\alpha]_D^{10}$ +35.4° in chloroform (*c* 1.13).

Found: C, 51.67; H, 7.53; OCH_3, 39.51; mol.

6) C. Araki, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **58**, 1362 (1937); E. G. V. Percival and J. C. Somerville, *J. Chem. Soc.* **1937**, 1615.
7) C. Araki, *J. Chem. Soc., Japan (Nippon Kwagaku Kwaishi)*, **61**, 775 (1940).
8) C. Araki, ibid., **65**, 533, 627 (1944).
9) S. Hirase, This Bulletin, **30**, 75 (1957).

wt., 394. Calcd. for $C_{12}H_{15}O_5(OCH_3)_5$: C, 51.77; H, 7.67; OCH_3, 39.35%; mol. wt., 394.4.

Conversion of the Methyl Glycoside (II) into the Dimethylacetal (I).—When methyl tetra-*O*-methyl-β-agarobioside (0.20 g.) obtained above was heated in 3% methanolic hydrogen chloride (20 ml.), the specific rotation of the solution changed from $+14°$ to $-29°$ within five minutes, at the end of which time the hydrochloric acid was removed by neutralization with silver carbonate and filtration. Evaporation of the filtrate gave a sirupy mixture of the dimethylacetal (I) and the starting material; yield, 0.20 g., $[\alpha]_D^{19}$ $-11.3°$ in water (*c* 0.53). The mixture was then resolved into the components on a column (2.7×11 cm.) of charcoal and Celite. The dimethylacetal was eluted from the column with 30% ethanol in water and crystallized from ether containing a few drops of petroleum ether; yield, 0.14 g., m. p. 88~89°C, $[\alpha]_D^{19}$ $-25.0°$ in water (*c* 0.80). Admixture with a sample of the dimethylacetal (I) described earlier showed no depression of the melting point. Subsequent elution of the column with 50% ethanol in water led to recovery of a small amount of the starting material.

Methyl Penta-*O*-methyl-β-agarobioside from II.—Methyl tetra-*O*-methyl-β-agarobioside (II) (0.30 g.) was methylated twice with methyl iodide (20 g.) and silver oxide (5 g.) in the usual manner. Extraction of the product with acetone followed by evaporation afforded methyl penta-*O*-methyl-β-agarobioside (0.30 g.), which was then recrystallized by dissolving in a small volume of ether and adding petroleum ether; m. p. 98~100°C, $[\alpha]_D^{19}$ $+48.1°$ in water (*c* 1.04). One of the present authors has reported m. p. 99~100°C and $[\alpha]_D^{27}$ $+48.32°$ in water for the methylated disaccharide derivative[3] previously isolated from methylated agarose. Admixture of the two showed no depression of the melting point.

Found: C, 52.85; H, 7.72; OCH_3, 45.68. Calcd. for $C_{12}H_{14}O_4(OCH_3)_6$: C, 52.93; H, 7.90; OCH_3, 45.59%.

Tetra-*O*-methylagarobiose.—*a) From the Dimethylacetal (I).*—The dimethylacetal (I) (0.20 g.) in 0.02 N aqueous oxalic acid solution (20 ml.) was heated in a boiling water bath for one and a half hours, during which time the specific rotation of the solution changed from an initial value $-25°$ to a constant value $+12°$. The solution was neutralized with calcium carbonate, filtered and evaporated to a sirup, which was then extracted with acetone. Filtration and evaporation of the extract afforded tetra-*O*-methyl-agarobiose as glass; yield, 0.17 g., $[\alpha]_D^{13}$ $-15.1°$ (constant) in water (*c* 0.86), OCH_3 found: 41.65% (calcd. for $C_{12}H_{16}O_6(OCH_3)_4$: 42.07%). It was soluble in water and organic solvents except ether and petroleum ether. It slowly reduced the Fehling solution at room temperature and restored the color of Schiff's reagent. Attempt to prepare a crystalline aniline derivative was unsuccessful.

b) From methyl glycoside (II).—The methyl glycoside (II) (0.20 g.) was hydrolyzed with 0.02 N oxalic acid solution in a boiling water bath for one and a half hours, during which time the specific rotation of the solution changed from an initial value $+41°$ to a constant value $-12°$, the final value being in exact agreement with that observed for the hydrolysis of dimethylacetal (I). The eesulting tetra-*O*-methylagarobiose was isolated as glass in exactly the same manner as described above; yield, 0.19 g., $[\alpha]_D^{13}$ $-15.6°$ (constant) in water (*c* 0.64), OCH_3 found 41.69%.

The authors wish to express their hearty thanks to Mr. K. Arai for micro-combustion and to Mr. T. Itô for assistance.

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*The Kinetics of Substitution Reactions Involving Metal Complexes. III. Reaction between Copper(II) and Zinc-Ethylenediaminetetraacetate Complexes in Aqueous Solutions**

By Kiyoko KATO**

(Received October 12, 1959)

In the previous papers[1,2], the substitution reaction of copper(II) ions and lead-ethylenediaminetetraacetate (EDTA) complexes was reported. The rate of the reaction was followed by measuring the change of the polarographic diffusion current of copper(II) ions with the time. The reaction was found to proceed simultaneously through three different reaction paths.

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1) N. Tanaka, K. Kato and R. Tamamushi, This Bulletin, **31**, 283 (1958).
2) N. Tanaka and K. Kato, ibid., **32**, 1376 (1959).

under the experimental conditions, and the rate constants of the elementary reactions of those reaction paths were determined. The effect of acetate ions on the rate of the substitution reaction was explained quantitatively on the basis of the formation of acetato complexes of copper(II) and lead(II) and on the assumption that the substitution reaction proceeds only through the hydrated metal ions.

Since it seemed worth while to extend the study to the substitution reactions involving EDTA-complexes of other metal ions, the substitution reaction of copper(II) ions and zinc-EDTA complexes

$$Cu^{2+} + ZnY^{2-} \rightleftarrows CuY^{2-} + Zn^{2+}$$

was dealt with. The results are presented in this paper.

Experimental

The preparation of solutions of copper(II) nitrate and disodium ethylenediaminetetraacetate was described in the previous paper[1]. A solution of zinc nitrate was prepared by dissolving a known amount of pure zinc metal in reagent-grade nitric acid.

The rate of the reaction between copper(II) ions and zinc-EDTA complexes was followed by measuring the change with the time in the polarographic diffusion current of copper(II) ions in acetate buffer solutions. Current-time curves were obtained with a Shimadzu RP-2 pen-recording polarograph. The dropping mercury electrode described in the previous paper[1] was used. This had an m value of 1.27 mg./sec. and a drop time of 3.69 sec. in an air-free solution of 0.1 M potassium chloride at 25°C with open-circuit.

Measurements were made at 15 and 0°C in acetate buffers of pH 4.4 to 5.0 which contained 0.1 M of sodium acetate unless otherwise stated. The ionic strength was adjusted to be 0.2 with potassium nitrate. Gelatin was added as a maximum suppressor by 0.01% in concentration.

Results and Discussion

In the solution containing acetate ions less than 0.2 M in concentration, copper(II) forms mono- and diacetato complexes, whereas zinc(II) forms only a monoacetato complex[2]. Therefore, the overall substitution reaction of copper(II) ions and zinc-EDTA complexes in acetate buffer solution is represented by the equations

$$Cu^{2+} + 2\,OAc^- \rightleftarrows CuOAc^+ + OAc^- \rightleftarrows Cu(OAc)_2 \quad (1)$$

$$Cu^{2+} + ZnY^{2-} \rightleftarrows CuY^{2-} + Zn^{2+} \quad (2)$$

$$Zn^{2+} + OAc^- \rightleftarrows ZnOAc^+ \quad (3)$$

where Y^{4-} means a completely dissociated EDTA anion. Under the condition that both zinc ions and zinc-EDTA complexes are present in a large excess over copper(II) ions, the substitution reaction 2 can be simplified to

$$Cu^{2+} \underset{k^-}{\overset{k^+}{\rightleftarrows}} CuY^{2-} \quad (4)$$

The rate equation for reaction 4 is expressed as[2]

$$-\frac{d[Cu^{2+}]_{app}}{dt} = k^+[Cu^{2+}]_{app} - k^-[CuY^{2-}] \quad (5)$$

where $[Cu^{2+}]_{app}$ is the concentration of copper(II) that can be determined polarographically, and given by the equation

$$[Cu^{2+}]_{app} = [Cu^{2+}] + [CuOAc^+] + [Cu(OAc)_2] \quad (6)$$

Integrating Eq. 5,

$$\ln\{[Cu^{2+}]_{app} - [Cu^{2+}]_{e,app}\} = -(k^+ + k^-)t + \ln\{[Cu^{2+}]_{0,app} - [Cu^{2+}]_{e,app}\}$$

is obtained, where subscripts 0 and e denote the initial and the equilibrium conditions, respectively. At the equilibrium of the reaction, the relation

$$\frac{k^+}{k^-} = \frac{[CuY^{2-}]_e}{[Cu^{2+}]_{e,app}} \fallingdotseq K^{Cu}_{Zn,app}\frac{[ZnY^{2-}]_0}{[Zn^{2+}]_{0,app}}$$

may be satisfied, where $K^{Cu}_{Zn,app}$ represents the apparent equilibrium constant expressed as

$$K^{Cu}_{Zn,app} = \frac{[Zn^{2+}]_{e,app}[CuY^{2-}]_e}{[Cu^{2+}]_{e,app}[ZnY^{2-}]_e}$$

The values of $K^{Cu}_{Zn,app}$ were determined polarographically to be 76 at 15°C and 92 at 0°C in acetate buffer solutions which contained 0.1 M of sodium acetate.

The apparent rate constant, $k^+/[ZnY^{2-}]_0$, was obtained at varied pH's at two different concentrations of zinc ions but at constant concentration of other species present. In Fig. 1 the values obtained at 15°C are plotted against the hydrogen ion concentration. This clearly indicates that a linear relation exists between $k^+/[ZnY^{2-}]_0$ and $[H^+]$. A similar relation was also found at 0°C.

On the basis of the dependencies of the observed apparent rate constants on the concentration of uncomplexed zinc ions, which are identical to those of the substitution reaction of copper(II) ions and lead-EDTA complexes[1,2], the following mechanisms were set down for reaction 2:

$$(i)\quad Cu^{2+} + ZnY^{2-} \underset{}{\overset{k_1^+}{\rightleftarrows}} CuY^{2-} + Zn^{2+} \quad (7)$$

$$(ii)\quad ZnY^{2-} + H^+ \rightleftarrows ZnHY^- \quad (8a)$$

3) N. Tanaka and K. Kato, ibid., 33, 417 (1960).

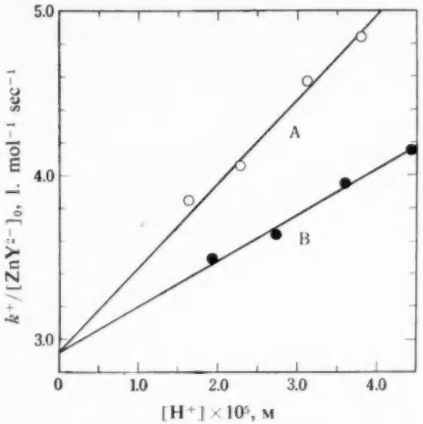

Fig. 1. $k^+/[ZnY^{2-}]_0$ as a function of the hydrogen ion concentration in acetate buffer–potassium nitrate solutions of ionic strength 0.2 at 15°C. Initial concentrations are: $[Cu^{2+}]_{0,app}=1.20\times10^{-4}$ M; $[ZnY^{2-}]_0=4.03\times10^{-3}$ M; $[Zn^{2+}]_{0,app}=1.12\times10^{-2}$ M (curve A) and 2.64×10^{-2} M (curve B). Concentrations of free acetate are: 0.096 M (A) and 0.091 M (B).

$$Cu^{2+} + ZnHY^- \overset{k_{II}^+}{\rightleftarrows} CuHY^- + Zn^{2+} \quad (8b)$$

$$CuHY^- \rightleftarrows CuY^{2-} + H^+ \quad (8c)$$

(iii) $$ZnY^{2-} + H^+ \rightleftarrows Zn^{2+} + HY^{3-} \quad (9a)$$

$$Cu^{2+} + HY^{3-} \overset{k_{III}^+}{\rightleftarrows} CuY^{2-} + H^+ \quad (9b)$$

As has been mentioned previously[2], the concentration which was actually measured polarographically was not the concentration of hydrated copper(II) ions but the sum of the concentrations of hydrated ions and acetato complexes. If it is assumed that the substitution reaction proceeds through only the hydrated metal ions which are in equilibrium with the acetato complexes, the apparent rate of the forward reaction ($v^+ = k^+[Cu^{2+}]_{app}$) determined polarographically is expressed as

$$v^+ = \left\{\frac{k_1^+ + k_2^+[H^+] + k_3^+[H^+]\dfrac{1+K_{ZnAOc}[OAc^-]}{[Zn^{2+}]_{app}}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n}\right\} \times [Cu^{2+}]_{app}[ZnY^{2-}] \quad (10)$$

where

$$k_2^+ = k_{II}^+ K_{ZnHY}^H, \quad k_3^+ = k_{III}^+/(K_{ZnY}K_{HY}) \quad (11)$$

K_{ZnHY}^H represents the equilibrium constant of reaction 8a, K_{ZnY}, the formation constant of ZnY^{2-} and K_{HY}, the fourth dissociation constant of ethylenediaminetetraacetic acid. $K_{Cu(OAc)_n}$ and K_{ZnOAc} represent the overall formation constants of acetatocopper(II) and acetatozinc-(II) complexes, respectively.

From Eqs. 5 and 10, the relation

$$\frac{k^+}{[ZnY^{2-}]_0} = \frac{k_1^+ + k_2^+[H^+] + k_3^+[H^+]\dfrac{1+K_{ZnOAc}[OAc^-]}{[Zn^{2+}]_{0,app}}}{1+\sum_{n=1}^{2}K_{Cu(OAc)_n}[OAc^-]^n} \quad (12)$$

is obtained, where the initial concentrations, $[Zn^{2+}]_0$ and $[ZnY^{2-}]_0$, are substituted for $[Zn^{2+}]$ and $[ZnY^{2-}]$, respectively. Since both Zn^{2+} and ZnY^{2-} are present in the reaction mixture in a large excess over the concentration of copper-(II), the changes of their concentrations can be neglected.

The rate constants in Eq. 10 were calculated from the plots of $k^+/[ZnY^{2-}]_0$ against hydrogen ion concentration, which are tabulated in Table I. The values of K_{CuOAc}, $K_{Cu(OAc)_2}$ and K_{ZnOAc} used in this calculation were 41, 190 and 5.7, respectively. These were all determined polarographically at ionic strength 0.2 at 15°C[2]. The concentration of uncomplexed acetate in the solution was calculated by successive approximation.

Table I. Rate constants in Eq. 10 obtained experimentally at ionic strength 0.2 at various temperatures

Temp., °C	Rate constant, l. mol^{-1} sec^{-1}		
	k_1^+	k_2^+	k_3^+
0	5.2	3×10^4	7.1×10^2
15	19	5×10^4	2.1×10^3

The rate constants of both elementary reactions 8b and 9b were calculated from the relations given in Eq. 11, using the values of K_{ZnHY}^H, K_{ZnY} and K_{HY} in Table II. The value of K_{ZnHY}^H which was determined by Schwarzenbach et al.[4] at 20°C at ionic strength 0.1 was used after correction for ionic strength with the Debye-Hückel equation. The values of K_{ZnY} at 15 and 0°C were obtained by dividing the value of K_{CuY} by those of K_{Zn}^{Cu}. As for K_{CuY}, the values obtained by Schwarzenbach et al.[4]

4) G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 37, 937 (1954).

were used after correction for temperature and ionic strength[2]. The equilibrium constants of reaction 2 at zero acetate concentration, K_{Zn}^{Cu}, used in this calculation were 320 at 15°C[3] and 310 at 0°C, the latter of which was estimated by extrapolation. The rate constants of three elementary reactions 7, 8b and 9b thus calculated are summarized in Table III.

TABLE II. EQUILIBRIUM CONSTANTS AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	$\log K_{ZnY}$	pK_{HY}	$\log K_{ZnHY}^{H}$
0	16.51	10.41	—
15	16.17	10.20	—
20	—	—	2.9

TABLE III. RATE CONSTANTS FOR REACTIONS 7, 8b AND 9b AT IONIC STRENGTH 0.2 AT VARIOUS TEMPERATURES

Temp., °C	Rate constant, l. mol^{-1} sec^{-1}		
	k_I^+	k_{II}^+	k_{III}^+
0	5.2	40	8.9×10^{8}
15	19	60	2.0×10^{9}

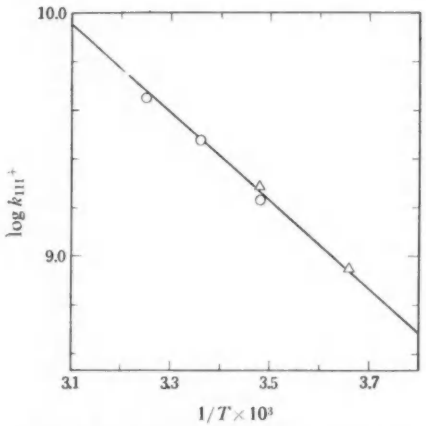

Fig. 2. The relation between the logarithm of rate constant and the reciprocal of absolute temperature for the reaction $Cu^{2+} + HY^{3-} \xrightarrow{k_{III}^+} CuY^{2-} + H^+$. ○ indicates the value in the reaction of copper(II) ions and lead-EDTA complexes and △, in the reaction of copper-(II) ions and zinc-EDTA complexes.

From these results, the rate constants expressed in the form of the Arrhenius equation were derived and the heats of activation and the entropies of activation were calculated for three elementary reactions 7, 8b and 9b. The results are given in Table IV.

The rate constants of reaction 9b were obtained at 15 and 0°C in this study as given in Table III. The logarithmic values of k_{III}^+ are plotted against the reciprocal of absolute temperature as shown in Fig. 2. The rate constants of the same reaction were previously obtained at 15, 25 and 35° in the study of the substitution reaction of copper(II) ions and lead-EDTA complexes[2]. They are also shown in Fig. 2, which are in good agreement with the present ones. This fact supports the validity of the method for the determination of the rate constants proposed in this series of papers.

From Eq. 10, it is predicted that the reaction rate decreases with the increase of acetate concentration. Using Eq. 12, the values of $k^+/[ZnY^{2-}]_0$ were calculated at various acetate concentrations with the rate constants given in Table I and

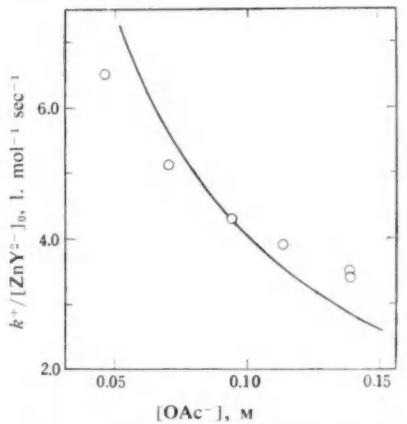

Fig. 3. $k^+/[ZnY^{2-}]_0$ as a function of the acetate concentration in acetate buffer–potassium nitrate solutions of pH 4.70 and ionic strength 0.2 at 15°C. Initial concentrations are:
$[Cu^{2+}]_{0,app} = 1.20\times10^{-4}$ M;
$[ZnY^{2-}]_0 = 4.03\times10^{-3}$ M;
$[Zn^{2+}]_{0,app} = 1.12\times10^{-2}$ M
—— indicates the theoretical curve and ○, the experimental value.

TABLE IV. RATE CONSTANTS, HEATS OF ACTIVATION AND ENTROPIES OF ACTIVATION FOR REACTIONS 7, 8b AND 9b

Reaction	Rate constant, expressed in l. mol^{-1} sec^{-1}	ΔH^+, kcal. mol^{-1}	ΔS^+, e. u.
$Cu^{2+} + ZnY^{2-} \rightarrow CuY^{2-} + Zn^{2+}$	$k_I^+ = 1.5\times10^{11}\exp(-13{,}000/RT)$	12	− 9.3
$Cu^{2+} + ZnHY^- \rightarrow CuHY^- + Zn^{2+}$	$k_{II}^+ = 6.3\times10^{5}\exp(-5{,}300/RT)$	4.7	−34
$Cu^{2+} + HY^{3-} \rightarrow CuY^{2-} + H^+$	$k_{III}^+ = 3.4\times10^{15}\exp(-8{,}200/RT)$	7.6	11

the formation constants of the acetato complexes. In Fig. 3, they are plotted against acetate concentration and compared with the values which were experimentally measured at various acetate concentrations, the other conditions being kept constant. The deviation of the experimental values from the calculated ones is considered as probably due to a contribution of the reactions in which acetatocopper(II) complexes participate.

Summary

The kinetic study of the substitution reaction of copper(II) and zinc-EDTA complexes in acetate buffer solutions was carried out with the same procedure as reported previously[1,2]. The reaction was found to proceed simultaneously through three different reaction paths under the experimental conditions. The rate constants for three elementary reactions of those reaction paths were determined at 15 and 0°C, and the heats of activation and the entropies of activation for the reactions were calculated.

The author wishes to express her hearty thanks to Professor Nobuyuki Tanaka for his guidance and encouragement in the course of this work.

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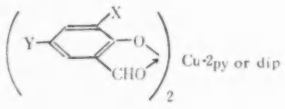
The Addition Compounds of Bis-salicylaldehyde Copper(II) and its Derivatives with Pyridine and α,α'-Dipyridyl. II. Some Studies on the Structures

By Yoneichiro MUTO

(Received September 28, 1959)

There are studies by several investigators reporting that copper(II) can form a complex with coordination numbers higher than four[1]. In the first paper[2] of this series, the author has reported the isolation of the addition compounds of bis-salicylaldehyde copper(II) and a number of its derivatives with pyridine or α, α'-dipyridyl having Formula I.



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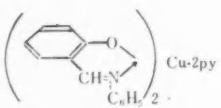


II

(X: H, NO_2; Y: H, Br, NO_2; py: Pyridine; dip: α, α'-Dipyridyl).

Although a hexa-coordinated octahedral configuration has been considered for bis-pyridine-bis-salicylaldehyde nickel by magnetochemical study[3], it is not definitely confirmed whether or not the copper atoms of these addition compounds are coordinated with six donors as yet. This paper presents some studies undertaken in order to investigate the structures of these addition compounds.

Spectrophotometric Studies.—Recently, Waters and Hall[4] have suggested that bis-salicylaldehyde copper(II) is solvated in coordinating solvents such as pyridine to give a penta- or hexa-coordinated copper(II) complex from the spectral change in various solvents. On the other hand, Charles[5] has shown that the spectra of some bis-*N*-*n*-alkylsalicylaldimine copper(II) in pyridine are similar to those in dioxane or toluene, although this is not the case with the corresponding nickel complexes. Therefore, he has concluded that no specific interaction (to form hexa-coordinated complexes) is present between the complexes and pyridine. However, the present author has observed that brown

1) H. B. Jonassen, R. E. Reeves and L. Sgal, *J. Am. Chem. Soc.*, **77**, 2748 (1955); S. Kirschner, ibid., **78**, 2372 (1956); D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, **1956**, 594; etc.

2) Y. Muto, This Bulletin, **31**, 56 (1958).

3) F. Basolo and W. R. Matoush, *J. Am. Chem. Soc.*, **75**, 5663 (1953).

4) T. N. Waters and D. Hall, *J. Chem. Soc.*, **1959**, 1200.

5) R. G. Charles, *J. Am. Chem. Soc.*, **81**, 1793 (1959).

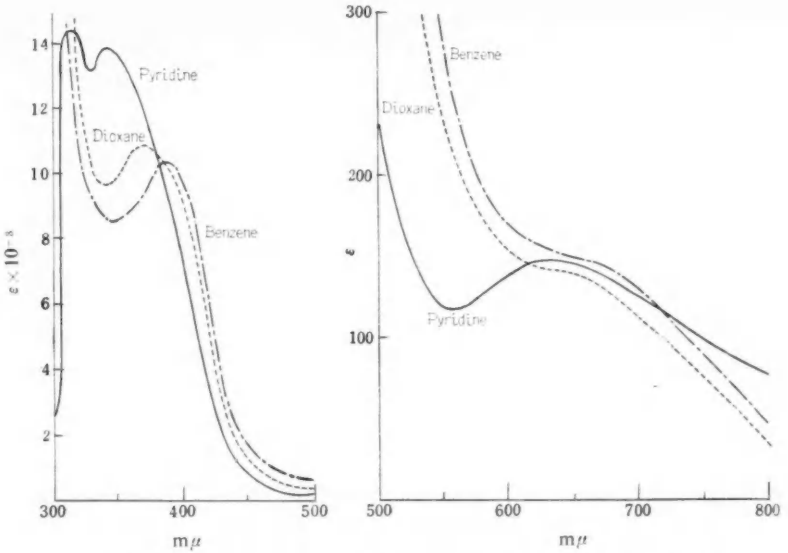


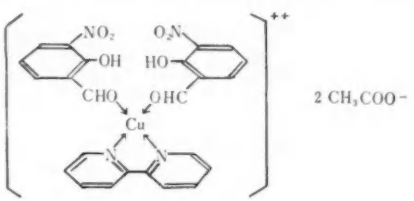
Fig. 1. Absorption spectra of bis-*N*-phenylsalicylaldimine copper(II).

bis-*N*-phenylsalicylaldimine copper(II) forms green crystals of a pyridinate having Formula II[2] and that its spectrum in pyridine is dissimilar to that in dioxane or benzene (Fig. 1). These facts confirm the formation of a hexa-coordination of the copper atom.

In addition, the author has observed that the absorption bands of bis-salicylaldehyde copper (II), a number of its derivatives, and bis-acetylacetone copper(II) in pyridine appear at longer wavelengths than those in dioxane (Figs. 2 and 3 and Table I). Probably, this indicates that the bands shift toward the longer wavelength side, owing to the formation of the hexa-coordinated copper(II) complexes in pyridine*.

Some Behaviors of the Addition Compounds. —Assuming that the addition compounds prepared in this study are hexa-coordinated copper-(II) complexes, the bond between the fifth or sixth donor and the copper atom should be weak relatively, as has been guessed from the fact that the usual coordination number of copper(II) is four. Actually, some of the pyridinates readily liberate pyridine. For example, bis-pyridine-bis-salicylaldehyde copper (II) lost pyridine gradually at room temperature. Also, the addition compounds with α, α'-dipyridyl were oxidized on heating in organic solvents such as ethanol to yield the derivatives of copper(II) monosalicylate[2], although α, α'-dipyridyl could be liberated from them with difficulty. This fact shows that probably the CHO → Cu bond is weak as compared with the N → Cu bond (in which N is a nitrogen atom of α, α'-dipyridyl). Namely, the CHO → Cu bond would be broken on heating in organic solvents, and then the aldehyde group would be oxidized, as benzaldehyde readily undergoes oxidation to benzoic acid in the presence of air.

Addition Compounds of α, α'-Dipyridyl-bis-3-nitrosalicylaldehyde Copper(II). — Among the addition compounds prepared in this study, only α, α'-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) formed further addition compounds with chloroform, picric acid and acetic acid. Although no direct evidence has yet been afforded to elucidate the structures of these



III

* It has been noticed by several investigators[6-8] that the absorption bands (from the near infrared to the near ultraviolet) of copper(II) complexes generally appear at longer wavelengths for hexa-coordinated complexes than for tetra-coordinated ones.

6) J. Bjerrum, C. J. Ballhausen and C. K. Jergensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

7) H. Ito, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **77**, 1395 (1956).

8) G. Gordon and R. K. Birdwhistell, *J. Am. Chem. Soc.*, **81**, 3567 (1959).

addition compounds by physical methods such as X-ray analysis, Formula III has been presumed for the acetate for the following reasons. First, it was observed that α,α'-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) could not be oxidized by heating in organic solvents and that α,α'-dipyridyl and 3-nitrosalicylaldehyde could be liberated from this complex with difficulty by the action of acetic acid, although other addition compounds with α,α'-dipyridyl were decomposed to give α,α'-dipyridyl-copper(II)-acetate. From these results, it seems that CHO→Cu and N→Cu bonds are relatively strong. Secondly, it seems that the bond between copper and phenolic oxygen in α,α'-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) has an ionic character to a considerable extent owing to the presence of a nitro and an aldehyde group at the ortho positions. Also, it has been observed that relatively strong acids such as picric acid or acetic acid add to the complex, while very weak acids such as phenol or cresol do not do so**. Therefore, it is possible that the complex forms a salt as shown in III.

TABLE I. ABSORPTION MAXIMA OF BIS-SALICYLALDEHYDE COPPER(II) DERIVATIVES IN THE VISIBLE REGION

Substituent	Solvents: Dioxane	Pyridine	(Addition compounds with α,α'-dipyridyl) Pyridine
5-Methyl	675 (1.71)	750 (2.04)	
None	670 (1.70)	740 (2.02)	700 (1.97)
5-Chloro	621 (1.62)	759 (1.95)	
5-Bromo	655 (1.93)	756 (2.27)	
3-Nitro-5-methyl	638 (1.65)	760 (1.92)	720 (1.97)
3-Nitro	670 (1.60)	710 (1.81)	704 (1.84)
5-Nitro	619 (?)	660 (2.45)	636 (2.40)
3,5-Dinitro	645 (?)	675 (2.37)	
Salicylaldehyde-ethylenedimine	576 (2.55)	602 (2.53)	
Bis-acetyl-acetone	612 (1.57)	654 (1.88)	

The values in parentheses are the logarithms of molar extinction coefficients ($\log\varepsilon$) at the maxima. The value marked with a question mark could not be determined accurately owing to the slight solubility of the complex in dioxane.

Experimental

Spectrophotometric Measurements.—Bis-salicylaldehyde copper(II), its derivatives and bis-acetylacetone copper(II) were prepared by conventional methods. The addition compounds with α,α'-dipyridyl were prepared by the method described in the first paper[2] of this study. Although bis-*N*-phenylsalicylaldimine copper(II) was very soluble in various organic solvents, other complexes were soluble in pyridine, slightly soluble in dioxane, and soluble with difficulty in other common organic solvents.

The absorption spectra were determined at 25 ±1°C with a Hitachi spectrophotometer (model EPU-2A) using 1 cm. quartz cells. The concentration of the complexes in solutions ranged from 5×10^{-5} to 3×10^{-3} mol. per liter depending upon the degree of absorption.

Preparation of additon compounds of α,α'-dipyridyl-bis-3-nitrosalicylaldehyde copper(II) with chloroform, picric acid, and acetic acid.—1) Cu·[O·$C_6H_3(NO_2)$·CHO]$_2$·dip·$CHCl_3$.—α,α'-Dipyridyl-bis-3-nitrosalicylaldehyde copper(II) (yellow-brown crystals) (0.6 g.) was dissolved in chloroform (30 ml.) and the resulting brown solution was filtered. The filtrate was allowed to stand overnight in air at room temperature; meanwhile the addition compound crystallized in green prismatic crystals. It was purified by repeated recrystallization from chloroform.

Found: C, 44.67; H, 2.85; N, 8.17; Cu, 8.59; $CHCl_3$, 17.82. Calcd. for $C_{14}H_8O_8N_2$·Cu·$C_{10}H_8N_2$·$CHCl_3$: C, 44.73; H, 2.55; N, 8.35; Cu, 8.56; $CHCl_3$, 17.78%.

Both α,α'-dipyridyl-bis-3-nitrosalicylaldehyde cobalt(II) and the corresponding nickel complex prepared by a method of synthesis similar to that employed for the copper(II) complex formed no addition compound with chloroform.

The cobalt complex was isolated in the form of red crystals.

Found: N, 10.16; Co, 10.82. Calcd. for $C_{14}H_8O_8N_2$·Co·$C_{10}H_8N_2$; N, 10.24; Co, 10.77%.

The nickel complex was isolated in the form of orange crystals.

Found: N, 10.29; Ni, 10.56. Calcd. for $C_{14}H_8O_8N_2$·Ni·$C_{10}H_8N_2$; N, 10.24; Ni, 10.73%.

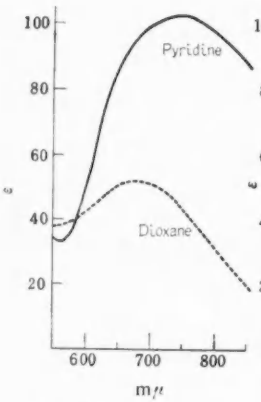


Fig. 2. Absorption spectra of bis-salicylaldehyde copper(II).

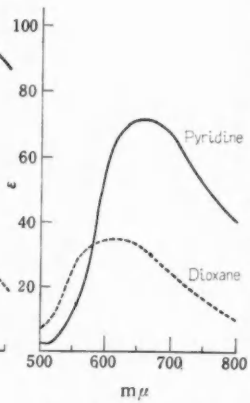


Fig. 3. Absorption spectra of bis-acetylacetone copper(II).

** Although it has been observed that *p*-nitrophenol add to the complex, the addition compound can not be isolated in the pure state.

2) $Cu \cdot [O \cdot C_6H_3(NO_2) \cdot CHO]_2 \cdot dip \cdot HO \cdot C_6H_2(NO_2)_3$.—*α*, *α*'-Dipyridyl-bis-3-nitrosalicylaldehyde copper(II) (0.3 g.) was added to 50 ml. of ether containing 0.2 g. of picric acid. The mixture was refluxed on a water bath for half an hour, meanwhile the addition compound crystallized in green prismatic crystals. The separated crystals were washed with ether repeatedly and then dried in a desiccator over sulfuric acid.

Found: C, 46.40; H, 2.71; N, 12.47; Cu, 8.16. Calcd. for $C_{14}H_8O_8N_2 \cdot Cu \cdot C_{10}H_8N_2 \cdot C_6H_3O_7N_3$: C, 46.13; N, 12.55; Cu, 8.15%.

3) $Cu \cdot [O \cdot C_6H_3(NO_2) \cdot CHO]_2 \cdot dip \cdot (CH_3COOH)_2$.—*α*, *α*'-Dipyridyl-bis-3-nitrosalicylaldehyde copper-(II) (0.6 g.) was dissolved in a mixture of ether (20 ml.) and acetic acid (3 ml.) and the resulting solution was filtered. When 30 ml. of ether was added to the filtrate, the addition compound precipitated in green prismatic crystals. The crystals were separated, washed with ether repeatedly, and then dried in a vacuum desiccator over sulfuric acid.

Found: C, 49.76; H, 3.89; N, 8.23; Cu, 9.26; CH_3COOH, 17.73. Calcd. for $C_{14}H_8O_8N_2 \cdot Cu \cdot C_{10}H_8N_2 \cdot C_4H_6O_4$: C, 50.04; H, 3.60; N, 8.34; Cu, 9.45; CH_3COOH, 17.87%.

The author is grateful to Mr. Michio Shido of Kyushu University for carrying out the elementary analysis of the compounds prepared.

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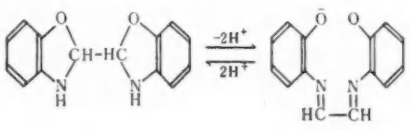
On the Structure of Condensation Products of o-Aminophenols with α-Dicarbonyl Compounds. III. Copper Chelates of 2, 2'-Bibenzoxazoline Derivatives

By Ichiro MURASE

(Received October 12, 1959)

In previous papers[1,2], the condensation products of *o*-aminophenols (2 mol.) with *α*-dicarbonyl compounds (1 mol.) were determined to have the structure of 2, 2'-bibenzoxazolines (I). In addition, 2, 2'-bibenzoxazoline tautomerized to the corresponding Schiff base (II) in ethanol solution on addition of alkali, the formation of its metal chelates being explained by the scheme indicated below. The structure of metal chelates was thus in agreement with the one stated by Bayer[3] as the derivatives of glyoxal bis-(2-hydroxy anil) (III).



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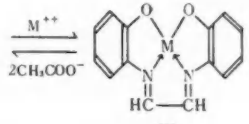
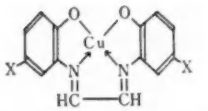


III

Here, the reaction of copper acetate with 2, 2'-bibenzoxazoline derivatives was conducted, obtaining copper chelates of 5, 5'-dinitro (IV), 5, 5'-dimethyl (V) and 5, 5'-dichloro (VI) derivative as deep violet or blue amorphous powder.



IV, X=NO_2 V, X=CH_3 VI, X=Cl

The absorption spectra in ethanol of these compounds were taken by the method indicated in the experimental part and they are shown in Fig. 1, where ε of each copper chelate was expediently calculated by means of concentrations of bibenzoxazolines dissolved.

Each spectrum did not represent the true feature of the copper chelate itself since the solution consisted of equilibrium mixture of bibenzoxazoline and copper chelate as suggested from the above scheme. However, the band at

1) I. Murase, This Bulletin, **32**, 827 (1959).
2) I. Murase, ibid., **33**, 59 (1960).
3) E. Bayer, *Ber.*, **90**, 2325 (1957).

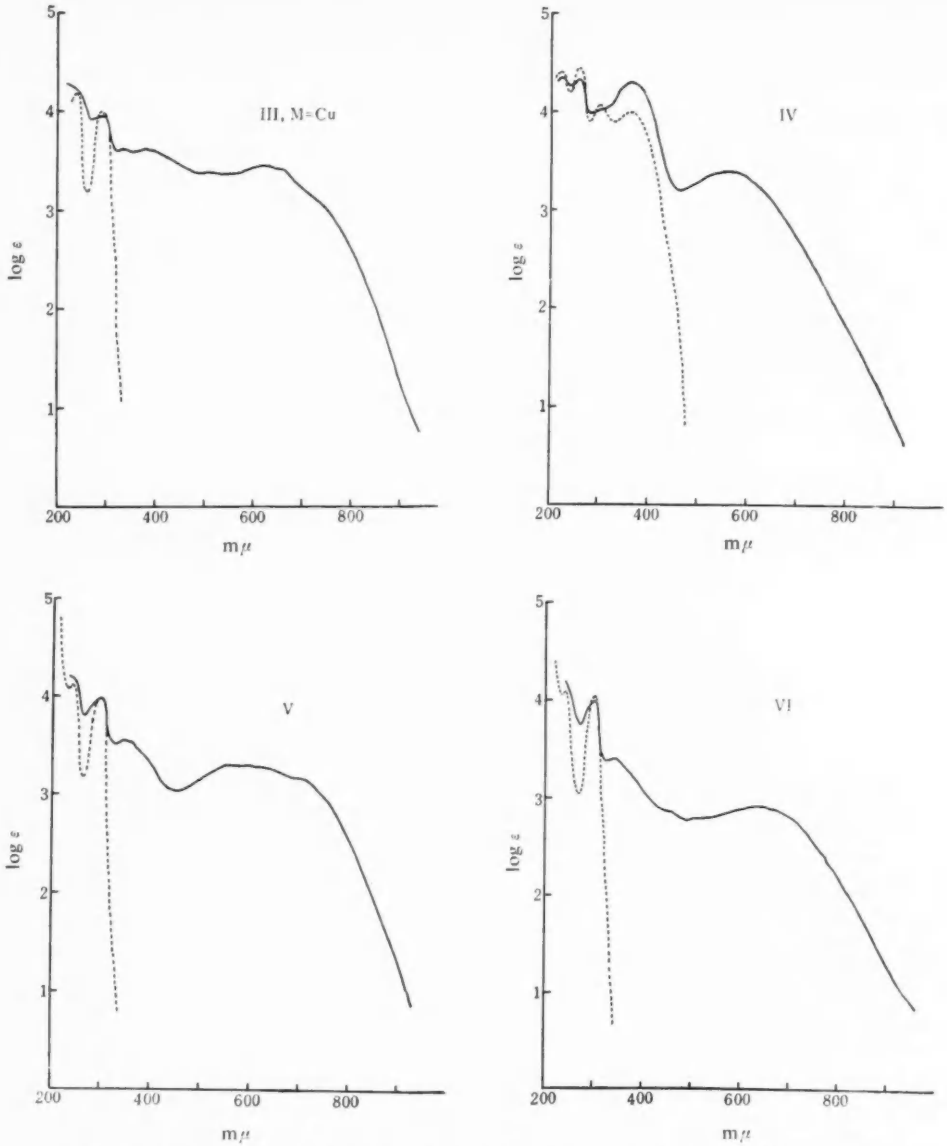


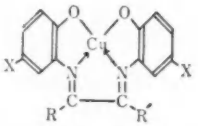
Fig. 1. Ultraviolet and visible absorption spectra of copper chelates of 2,2'-bibenzoxazoline and its derivatives in ethanol, ——; copper chelate, ------; parent bibenzoxazoline or its derivative.

500~600 mμ in each spectrum should be due to metal-ligand linkage and it resembles the authentic one of glyoxal bis-(2-hydroxy anil)-copper (Fig. 1, III, M=Cu), the solution of which was prepared also in the same manner as other chelates. Therefore, it has been assumed from those spectra that these copper chelates have structures IV—VI.

In the case of 2-substituted and 2,2'-disubstituted derivatives of 2,2'-bibenzoxazoline such as 2-methyl-, 5,5'-dinitro-2-methyl-, 2-methyl-2'-ethyl-2,2'-diethyl- and 2-methyl-2'-phenyl-bibenzoxazoline, with the exception of 2,2'-dimethyl derivative, deep violet or blue colored solutions

were obtained by addition of copper acetate to their ethanol solutions. On concentration of these colored solutions, no copper chelates were isolated, instead the oxazolines were recovered unchanged. However, the presence of the chelates in solution was suggested by their coloration and was revealed by their absorption spectra which are shown in Fig. 2, where ε of each copper chelate was calculated in the same manner as in Fig. 1.

These spectra resemble those in Fig. 1 in having absorption bands at 500~600 mμ, though their absorption intensities varied with substituents in 2, 2'-positions. Thus, the presence of copper chelates in solution of similar structures VII—XII has been recognized.



VII, R=CH_3, R'=X=H
IIX, R=CH_3, R'=H, X=NO_2
IX, R=R'=CH_3, X=H
X, R=CH_3, R'=C_2H_5, X=H
XI, R=R'=C_2H_5, X=H
XII, R=CH_3, R'=C_6H_5, X=H

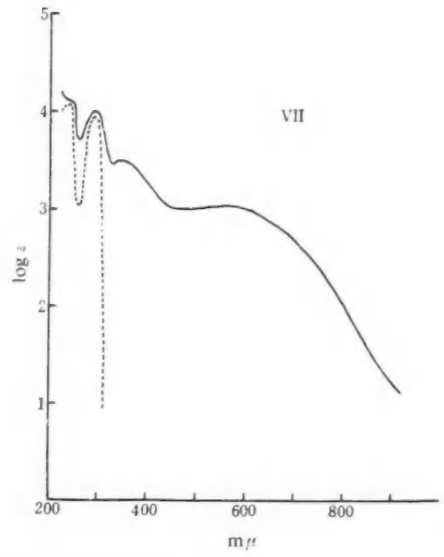
The reason why these copper chelates could not be isolated may be that their formation constant is considerably small. Since the formation constant in each case should be introduced from overall equilibrium consisting of oxazoline, Schiff base and chelate, the proportion of the tautomeric form of oxazoline in the mixture should be considered to be very small.

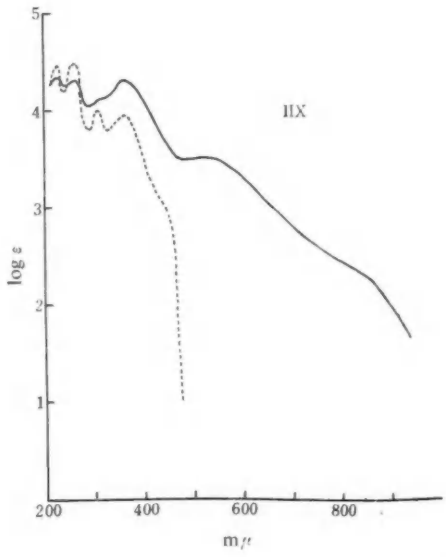
With respect to the condensation product of *o*-aminophenol with diacetyl, Bayer explained its inability to form metal chelate as the result of the hindrance of methyl groups in diacetyl bis-(2-hydroxy anil), but the author previously suggested, from the spectroscopic behavior toward alkali, that 2, 2'-dimethyl-2, 2'-bibenzoxazoline does not tautomerize to diacetyl bis-(2-hydroxy anil) and forms no metal chelates[1].

Apparently no deep coloration was observed when copper acetate was added to this compound in ethanol. Nevertheless, in this case also, the presence of the chelate in solution was suggested from the careful observation of its spectrum (Fig. 2, IX); an absorption maximum was observed at 560 mμ though in very weak intensity. Thus, it was found that 2, 2'-dimethyl-2, 2'-bibenzoxazoline still possesses a tendency of tautomerism and of formation of copper chelate in solution.

Thus, it is concluded that 2, 2'-bibenzoxazolines acquire an ability of metal chelate formation through tautomerism, which is most remarkable in the case of 2, 2'-unsubstituted derivatives and is hindered by substituents at 2, 2'-position, among which the methyl group is most effective and the phenyl group is not so much.

In the case of carboxy derivatives of bibenzoxazoline, it is interesting to note that 5, 5'-dicarboxy derivative gave reddish violet precipitates on reacting with an equimolar amount





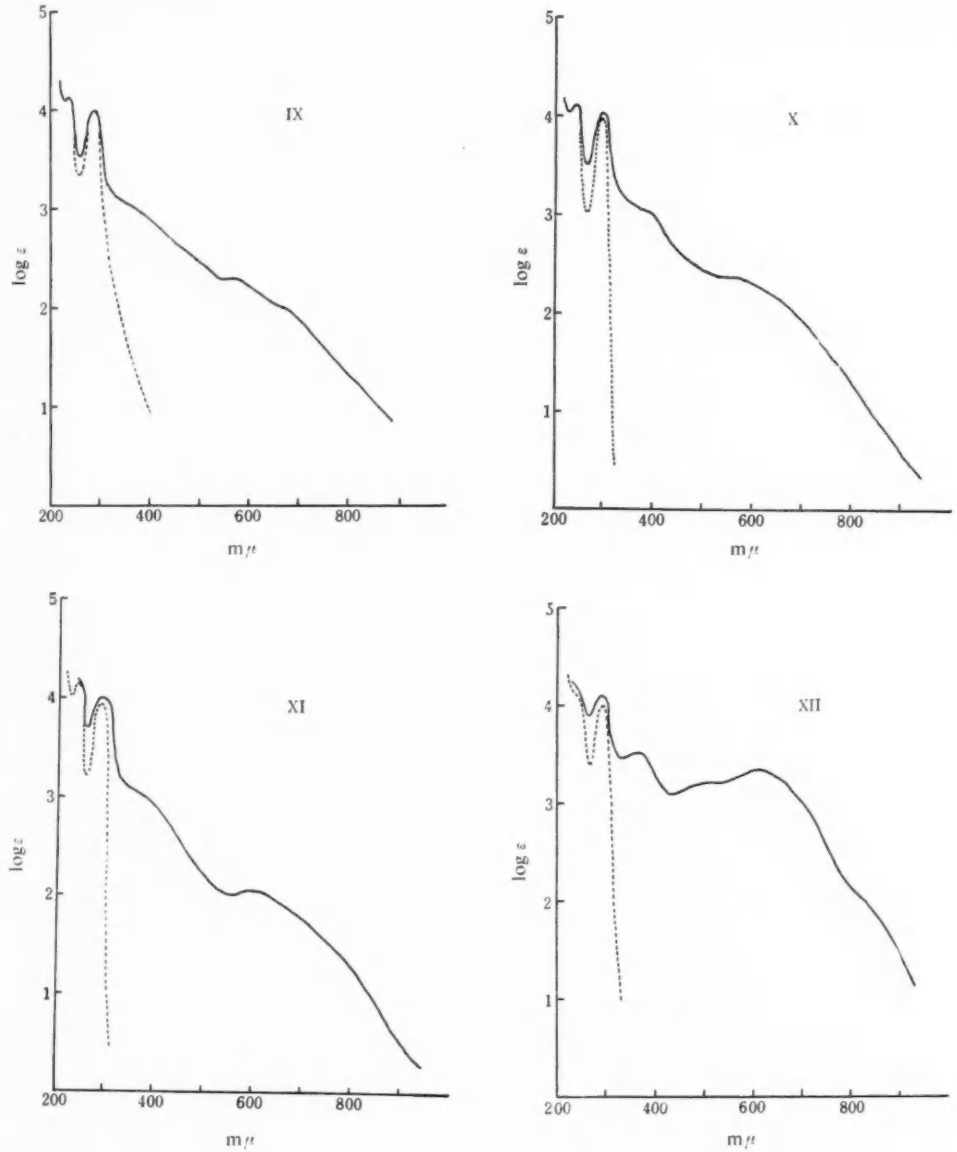


Fig. 2. Ultraviolet and visible absorption spectra of copper chelates of 2, 2'-bibenzoxazoline derivatives in ethanol, ——; copper chelate, ------; parent bibenzoxazoline derivative.

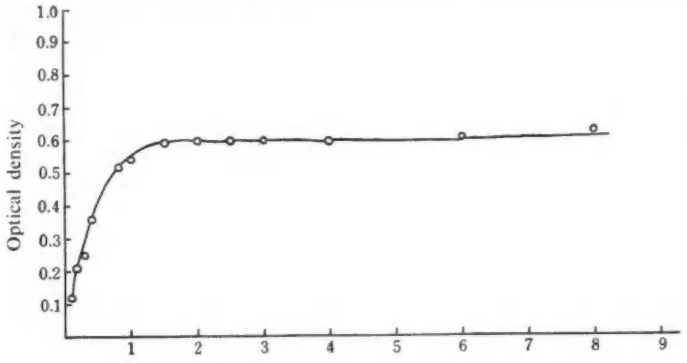


Fig. 3. Optical densities at 540 mμ of various solutions with excess 2-methyl-bibenzoxazoline present: Cu-acetate = 9.99×10^{-5} M.

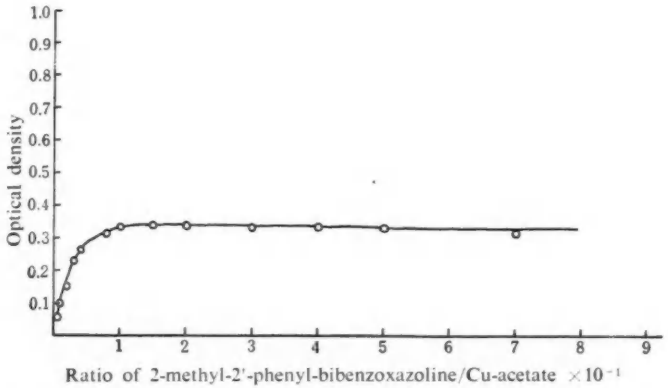
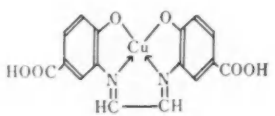
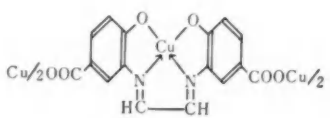


Fig. 4. Optical densities at 600 mμ of various solutions with excess 2-methyl-2'-phenyl-bibenzoxazoline present: Cu-acetate = 4.99×10^{-5} M.

of copper acetate. Since a part of the precipitates was soluble in sodium hydrogen carbonate solution with a blue-violet coloration, the precipitates should contain copper chelate of structure XIII* in which the carboxyl groups are free and the copper atom is coordinated with the Schiff base ligand in the same manner as the other chelates. When this dicarboxy derivative reacted with bimolar amounts of copper acetate, blue-violet precipitates were obtained. This substance was insoluble in sodium hydrogen carbonate solution and consisted of two copper atoms to one molecule of ligand. The structure should be given as XIV in which one copper atom chelates and the other combines as carboxylate.



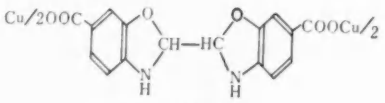
XIII



XIV

* The precipitates were treated with sodium hydrogen carbonate solution and the soluble part was reprecipitated by neutralization with acetic acid. The substance obtained did not show reasonable analytical results, possibly due to partial decomposition by this treatment.
Found: C, 44.26; H, 3.48; N, 7.04; Cu, 16.07. Calcd. for $C_{16}H_{16}N_2O_6 \cdot 2H_2O$: C, 45.13; H, 3.31; N, 6.58; Cu, 15.39%.

On the other hand, 6, 6′-dicarboxy derivative gave green precipitates with copper acetate. The substance may have the structure of simple salt of bibenzoxazoline carboxylic acid (XV), because they were insoluble in sodium hydrogen carbonate solution and consisted of one copper atom to one oxazoline molecule. The structure may further be supported by its green color which is seen in ordinary copper carboxylates. It seems that the carboxyl groups at 6, 6′-positions prevent the ring opening of oxazoline to form the Schiff base.



XV

For the determination of metal-ligand proportion in metal chelate in solution, the molar ratio method is known[4]; it consists of the measurement of optical density at a typical wavelength at which an absorption is caused by metal chelate formation, the molar ratio of the ligand being varied to a constant metal ion concentration. If a formation constant of metal chelate is appreciably large, the optical density should reach a constant value at which the metal-ligand proportion is equivalent.

In the case of the above copper chelates, in which the metal-ligand ratio is naturally 1 : 1, the optical densities should be expected to give constant values over the range of more than this ratio.

The experiment was carried out on 2-methyl-bibenzoxazoline and 2-methyl-2′-phenyl-bibenzoxazoline**. The results are shown in Figs. 3 and 4, but they fell short of expectations.

The optical density of each solution gave almost constant value for ratios greater than 20. Since such poly-coordinate chelate is considered to be impossible, these curves should mean that stability constants of these copper chelates are small. Here again, it proved that the equilibrium between bibenzoxazoline and the Schiff base exists in favor of the former.

Experimental

Copper Chelate of 5, 5′-Dimethyl-2, 2′-bibenzoxazoline.—To a solution of 5, 5′-dimethyl-2, 2′-bibenzoxazoline (0.2 g.) in hot methanol (50 ml.), a solution of copper acetate (0.15 g.) in methanol (20 ml.) was added and the mixture was heated on a water bath for 30 min. The resulting deep violet-blue precipitates were centrifuged and washed with methanol and dried over phosphorus pentoxide in vacuo at 110°C.

Found: C, 55.43; H, 4.48; N, 7.98; Cu, 18.61. Calcd. for $C_{16}H_{14}N_2O_2Cu \cdot H_2O$: C, 55.24; H, 4.60; N, 8.04; Cu, 18.26%.

Copper Chelate of 5, 5′-Dichloro-2, 2′-bibenzoxazoline.—Prepared from 5, 5′-dichloro-bibenzoxazoline (0.2 g.) and copper acetate (0.13 g.) in the same manner as described in the case of the dimethyl derivative. Deep blue amorphous powder.

Found: C, 43.07; H, 2.71; N, 7.43; Cu, 15.96. Calcd. for $C_{14}H_8N_2O_2Cl_2Cu \cdot H_2O$: C, 43.26; H, 2.57; N, 7.20; Cu, 16.34%.

Copper Chelate of 5, 5′-Dinitro-2, 2′-bibenzoxazoline.—Prepared from 5, 5′-dinitro-bibenzoxazoline (0.5 g.) and copper acetate (0.4 g.) in the same manner as described in the case of the dimethyl derivative. Deep reddish violet crystalline powder.

Found: C, 41.12; H, 2.53; N, 13.55; Cu, 15.55. Calcd. for $C_{14}H_8N_4O_6Cu \cdot H_2O$: C, 40.97; H, 2.43; N, 13.65; Cu, 15.51%.

Copper Chelate of Copper-2, 2′-bibenzoxazoline-5, 5′-dicarboxylate.—To a solution of 5, 5′-dicarboxy-2, 2′-bibenzoxazoline (0.5 g.) in hot methanol (300 ml.), copper acetate (0.8 g.) in methanol (50 ml.) was added and the mixture was heated on a water bath for 1 hr. After cooling, resulting precipitates were filtered and washed with methanol and dried over phosphorus pentoxide in vacuo at 110°C. Deep blue-violet crystalline powder.

Found: C, 36.84; H, 3.00; N, 5.06; Cu, 24.91. Calcd. for $C_{16}H_8N_2O_8Cu_2 \cdot 4H_2O$: C, 36.71; H, 3.08; N, 5.35; Cu, 24.28%.

Copper-2, 2′-bibenzoxazoline-6, 6′-dicarboxylate.—To a suspension of 6, 6′-dicarboxy-2, 2′-bibenzoxazoline (0.2 g.) in ethanol (100 ml.), a solution of copper acetate (0.12 g.) in ethanol and 2 drops of acetic acid were added and the mixture was heated on a water bath for 4 hr. The crystals were gradually diminished and green precipitates were formed. After standing over-night, they were filtered and washed with ethanol and dried over phosphorus pentoxide in vacuo at 60°C.

Found: C, 45.62; H, 3.49; N, 6.21; Cu, 14.96. Calcd. for $C_{16}H_{10}N_2O_8Cu \cdot 2H_2O$: C, 45.13; H, 3.31; N, 6.58; Cu, 15.39%.

Absorption Spectra.—The copper chelates III~VI, when once precipitated, were very difficult to dissolve in ethanol. To obtain the ultraviolet and visible absorption spectra in ethanol of these compounds, a method was devised in the preparation of the solution. To ethanol solutions of bibenzoxazolines (ca. 1/5000~1/10000 M), equimolar amounts of copper acetate in ethanol were added and the solutions were heated at 70°C for ten minutes and cooled to room temperature. The coloration of each solution reached almost a maximum by this treatment and further heating resulted in decolorization by decomposition, thus clear colored solutions containing copper chelates being obtained.

4) S. Miyakawa and T. Uemura, This Bulletin, **24**, 25 (1951); R. P. Yaffe and A. F. Voigt, *J. Am. Chem. Soc.*, **74**, 2503 (1952).

** Since their own spectra have no absorption at a visible region (refer to Fig. 2, VII and XII), the optical densities could be observed without any correction. For the measurements, the solution were prepared in the same manner as the case of the measurement of their spectra and the concentration of coppr acetate was used in place of the copper ion concentration to avoid the ambiguity of the latter in ethanol.

In the case of VII—XII, the solutions were prepared also in the same manner as indicated above. The measurement of absorption spectra and optical densities in the molar ratio method were carried out using a Hitachi EPU-2A spectrophotometer with a 10 mm. quartz cell.

The author wishes to express his thanks to Professor Tokuichi Tsumaki and Professor Takeichi Nishikawa for their exceedingly kind directions of this work. The author also thanks Mr. Michio Shido and Miss Sachiko Indo for the microanalysis.

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Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. X. Benzaldehyde, Acetophenone and Related Compounds

By Hiroshi SUZUKI

(Received October 30, 1959)

Benzaldehyde and Acetophenone

In the near ultraviolet absorption spectrum of benzaldehyde as well as that of acetophenone four band systems appear. The weakest band, which appears at about 320 mμ with the molecular extinction coefficient of the order of ten, is regarded as an $n \rightarrow \pi^*$ transition in the carbonyl group (R-band). The weak band with fine structure, which appears in the range between 270 and 290 mμ with the molecular extinction coefficient of about 1000～2000, is considered to correspond to the $A_{1g} \rightarrow B_{2u}$ transition in benzene, and therefore, to the "hidden transition" at about 275 mμ in biphenyl[1] (B-band, or Benzenoid band). The band at about 200 mμ is considered to correspond to the $A_{1g} \rightarrow B_{1u}$ transition in benzene. The strongest band at near 240 mμ, whose molecular extinction coefficient is about 15000, has been interpreted by Tanaka, Nagakura, and Kobayashi[2] as the "intramolecular charge-transfer absorption", which may be considered as the conjugation band (K-band). (The notation of the bands shown in parentheses is according to Gillam and Stern[3]). The present study is mainly concerned with the last "conjugation band".

O'Shaughnessy and Rodebush[4] found formerly that the introduction of two methyl groups into the ortho positions of acetophenone exerts a marked influence on the absorption spectrum, a fact which was explained in terms of the steric effect. Braude and his coworkers[5-8] have stated, on the basis of their classification of steric effects in ultraviolet absorption spectra, that *o*-methylated acetophenones and benzaldehydes show the steric effects of type I, i.e. the steric effects which give rise to decreases in absorption intensity alone without causing any wavelength displacement of the bands. According to them, the steric effect of this type occurs when steric interaction is relatively weak, i.e. when the steric repulsion energy for the planar conformation is less than 3 kcal./mol., and is produced by "transitions between nonplanar ground states and uniplanar (or near-planar) excited states".

On the basis of the above mentioned view, they have applied their postulated relation between the intensity of the conjugation band and the angle of twist of the "single" bond to

1) H. Suzuki, This Bulletin, **32**, 1340 (1959).
2) J. Tanaka, S. Nagakura and M. Kobayashi, *J. Chm. Phys.*, **24**, 311 (1956).
3) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 2nd. Ed., Edward Arnold Publishers, Ltd., London (1957), p. 141 and p. 262.
4) M. T.O'Shaughnessy and W. H. Rodebush, *J. Am. Chem. Soc.*, **62**, 2906 (1940).
5) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).
6) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.
7) E. A. Braude and E. S. Waight, "Progress in Stereochemistry", I, (edited by W. Klyne), Butterworths Scientific Publications, London (1954), p. 144 ff.
8) E. A. Braude, "Determination of Organic Structures by Physical Methods", (edited by E. A. Braude and F. C. Nachod), Academic Press, Inc., Publishers, New York (1955), p. 172 ff.

o-substituted benzaldehydes and acetophenones, and found that in the aldehydes the calculated angle of twist θ (i.e. the interplanar angle between the benzene ring and the carbonyl group) is about 20° in the presence of either the one or the two *o*-methyl groups, and that in the ketones the calculated interplanar angle is about 35° in the presence of the one, and about 60° in the presence of the two, *o*-methyl groups. In the calculations, they have taken the parent compounds, benzaldehyde and acetophenone, as the planar reference compounds for the corresponding derivatives. That is, they have assumed that there is no significant steric hindrance to the coplanarity of the molecular configuration with acetophenone as well as benzaldehyde. This assumption would be considered to be supported by the fact that, according to Braude and others, both the compounds exhibit their conjugation bands at almost the same wavelength (242 mμ, in hexane).

On the other hand, as will be shown in the succeeding part of this series, α-methylstyrene exhibits the conjugation band at an appreciably shorter wavelength than its parent compound, styrene. That is, it may be said that the α-methyl group in this system exerts the "steric effect of type 2" defined by Braude and others, i.e. the steric effect which causes not only a decrease in the intensity of the conjugation band but also a hypsochromic wavelength displacement of the band. Thus, the most probable configuration of α-methylstyrene is inferred to be nonplanar. While the geometry of the relevant part of benzaldehyde is considered to be similar to that of styrene, that of acetophenone is considered to be similar to that of α-methylstyrene. Accordingly, it is expected that the steric effects in acetophenone and in α-methylstyrene are likely to be very similar. That is, it is presumed, contrary to the opinion of Braude and others, that there should be appreciable steric interaction between the methyl group and the phenyl group in the planar conformation of acetophenone, and that, consequently, the most probable configuration of the molecule is not planar. According to Auwers and Eisenlohr[9], the value of the exaltation of molecular refraction, EM_D, for acetophenone (+0.52) is considerably smaller than the value for benzaldehyde (+0.80). This fact may be considered to indicate that acetophenone is less conjugated than benzaldehyde, and therefore, to support the above mentioned view.

It may be somewhat doubtful whether a deviation from the coplanar configuration results in a hypsochromic displacement of the "conjugation band" also in the present conjugated system, because the system containing a hetero-atom O is not quite analogous to the hydrocarbon conjugated systems (termed "normal") treated in the preceding parts of this series. Therefore, it seems to be necessary to make some comment on this point.

According to Nagakura and Tanaka[10], in the conjugated system C_6H_5–C=O the interaction between the lowest vacant orbtial of the carbonyl group (V_S) and the highest occupied orbital of benzene (H_B) is predominant, and to a first approximation the intense absorption bands in the wavelength region 230~260 mμ are regarded as due to the transition between the two new orbitals W_n and W_v which occur by the interaction between V_S and H_B. The new highest occupied orbital W_n is lower than H_B, and the new lowest vacant orbital W_v is higher than V_S. The energy separation between W_v and W_n will become greater when the interaction between V_S and H_B becomes greater. Accordingly, from this theory, it might be expected that a twist of the "single" bond between the phenyl group and the carbonyl group from the coplanar position would cause a bathochromic shift of the absorption band rather than a hypsochromic shift.

This surmise seems, however, to be denied by the fact that the absorption band maxima of 2-methylbenzaldehyde and of 2-methylacetophenone are at considerably shorter wavelengths than the corresponding 4-isomers. Especially, it is notable that the absorption maximum of 2-methylbenzaldehyde is at a shorter wavelength even than that of the 3-isomer. Thus, according to Braude and Sondheimer[6], the wavelengths (in mμ) of the absorption maxima of these compounds are as follows (figures in parentheses represent the molecular extinction coefficients): 4-methylbenzaldehyde, 251(15000) and 257 (12500); 3-methylbenzaldehyde, 245(13500) and 251(12000); 2-methylbenzaldehyde, 243(12500) and 251(13000); 4-methylacetophenone, 252 (15100); 2-methylacetophenone, 242(8700) and 245(8300). Since the electronic effect of an ortho-methyl group may be said to be approximately equivalent to that of a para-methyl group, it may be quite reasonable to consider the hypsochromic displacements observed above as mainly due to the steric effect of the ortho-methyl groups. Accordingly, it may be said that a deviation of the most probable conffiguration from the coplanarity causes a hypsochromic displacement of the "conjugation band" in the case of the conjugated system C_6H_5–C=O, just as in the cases of the normal conjugated systems. Therefore, from the foregoing consideration it may be expected that the conjugation band of acetophenone will be at a

9) K. v. Auwers and F. Eisenlohr, *Ber.*, **43**, 806 (1910).

10) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).

TABLE I. ABSORPTION MAXIMA OF BENZALDEHYDE, ACETOPHENONE AND BENZOPHENONE

Compound	Solvent	"Benzenoid band"		"Conjugation band"		Ref.
		λ, mμ	ε	λ, mμ	ε	
Benzaldehyde	Hp	288.9	890	248.1	8600	*a*
		280.6	1410	(240.5)	13400	
		273.8	1520	236.9	14100	
			[C-band :	(204.8)	18900]	
	Hx	289	1200	248	12500	5-8
		280	1400	242	14000	
	E	280	1500	244	15000	3
Acetophenone	Hp	286.2	1180	(245.5)	9690	*a*
		278.3	1480	238.5	13130	
		275.2	1460			
		271.4	1440			
	Hp	279	890	238	12600	2
	Hx			242	13000	5,7,8
	E	278	1000	242	11750	2
	E	279	1200	243	13200	6
	E	278	1100	240	13000	3
Benzophenone	Hp	[(286)]	1550	248.5	19550	*a*
		[(277)]	2540			

Solvent : Hp, *n*-heptane ; Hx, hexane ; E, ethanol. Wavelengths in parentheses denote inflections, and those in double parentheses denote very indistinct inflections. Ref. *a*, the present work.

shorter wavelength than that of benzaldehyde. In this connection, it may be of some interest that in the case of the conjugated system C_6H_5–C=N the "conjugation band" maximum of the acetophenone analogue is at a considerably shorter wavelength than the corresponding one of the benzaldehyde analogue. Thus, according to Braude and Sondheimer[6], the wavelengths of the absorption maxima of the semicarbazones of benzaldehyde and of acetophenone are 281 mμ (22000) and 270 mμ (20400), respectively.

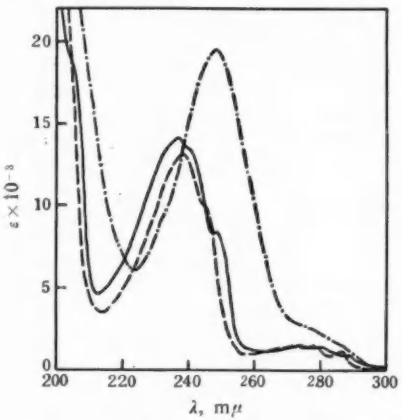

Fig. 1. Ultraviolet absorption spectra (in *n*-heptane): ——, benzaldehyde ; ----, acetophenone ; -·-·, benzophenone.

From this point of view, to re-examine the steric effect in acetophenone itself, the ultraviolet absorption spectra of acetophenone and of benzaldehyde in solutions in *n*-heptane have newly been measured. The results are shown in Fig. 1. In Table I, the data of the absorption maxima are summarized together with those found in the literature.

The conjugation bands of these compounds are not structureless, but have, though considerably diffuse, fine structures. The inflection at 245.5 mμ in the spectrum of acetophenone is at a shorter wavelength than the probably corresponding maximum at 248.1 mμ in the spectrum of benzaldehyde, in accordance with the expectation. On the other hand, the maximum at 238.5 mμ in the spectrum of acetophenone appears to correspond to the two bands at 240.5 and 236.9 mμ in the spectrum of benzaldehyde. Therefore, it seems somewhat doubtful which of the two bands of benzaldehyde is to be compared with the band of acetophenone.

p-Biphenylyl and 2-Fluorenyl Carbonyl Compounds

The author prepared *p*-phenylbenzaldehyde and *p*-phenylacetophenone as intermediates in the syntheses of *p*, *p'*-diphenylstilbene and its α, α'-dimethyl derivative, as described in the preceding part[11] of this series. In addition,

11) H. Suzuki, This Bulletin, 33, 410 (1960).

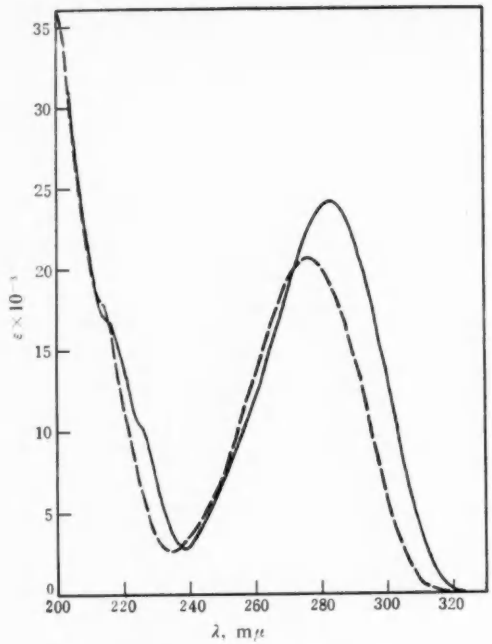

Fig. 2. Ultraviolet absorption spectra (in *n*-heptane): ——, *p*-phenylbenzaldehyde; ----, *p*-phenylacetophenone.

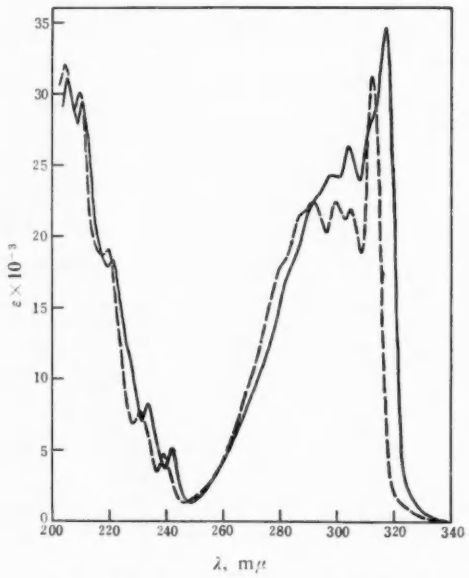

Fig. 3. Ultraviolet absorption spectra (in *n*-heptane): ——, 2-formylfluorene; ----, 2-acetylfluorene.

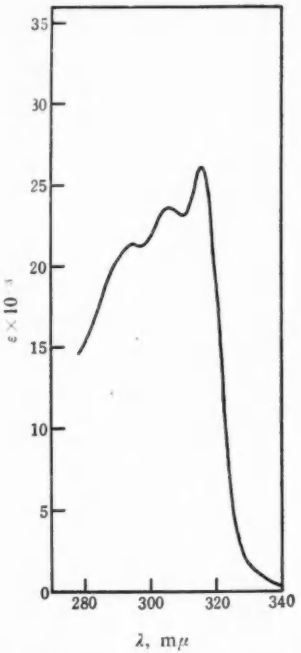

Fig. 4. Ultraviolet absorption spectrum of 2-acetylfluorene in benzene.

2-acetylfluorene and a compound which is considered to be probably 2-formylfluorene were prepared in attempts to prepare 1, 2-di-(2-fluorenyl)-ethylene and its 1, 2-dimethyl derivative. The absorption spectra of these analogues of benzaldehyde and of acetophenone seem to be of interest in connection with the above considerations. The spectra are shown in Figs. 2—4. In Table II, the data of the absorption maxima are summarized.

In the spectra of these compounds, the possible bands corresponding to the bands of benzaldehyde and of acetophenone in the range between 270 and 290 mμ are completely hidden by the intense conjugation bands. The bands appearing in the range between near 215 mμ and near 240 mμ are considered to be probably the ones due to transitions from the highest occupied orbital to the vacant orbitals localized in benzene rings whose energy is $-\beta$, or from the occupied orbitals localized in benzene rings whose energy is $+\beta$ to the lowest vacant orbital, analogously to the bands of stilbene and related compounds appearing in almost the same range[12,13]. It may be noteworthy that the bands at 200~210 mμ have about double the intensity of the corresponding band of benzaldehyde, in conformity

12) H. Suzuki, ibid., 33, 379 (1960).
13) H. Suzuki, ibid., 33, 389 (1960).

TABLE II. ABSORPTION MAXIMA OF *p*-BIPHENYLYL AND 2-FLUORENYL CARBONYL COMPOUNDS

Compound	Solvent	A-band		B-band		C-band	
		λ, mμ	ε	λ, mμ	ε	λ, mμ	ε
p-phenylbenzaldehyde	Hp	283.5	24150	[(226)]	10100		
				(215.5)	16900		
p-Phenylacetophenone	Hp	276.2	20650	(214.5)	17750	200.0	35700
2-Formylfluorene	Hp	317.2	34600	242.3	5050	210.5	29400
		(312.2)	28200	234.0	8220	205.2	31100
		304.4	26300	221.2	18320		
		297.7	24200				
		(293.5)	22900				
		[(285)]	18400				
2-Acetylfluorene	Hp	312.8	31200	239.3	4730	209.7	30500
		305.1	21850	231.1	7730	204.5	32000
		299.7	22400	219.8	19100		
		291.8	22450				
		(287.2)	21450				
		(280.9)	18050				
	B	315.8	26100				
		305.3	23650				
		294.8	21350				
		[(289.5)]	20200				

The notation of the bands is quite analogous to the one in the case of stilbenes in Part V of this series: A-band refers to the conjugation band. Solvent: Hp, *n*-heptane; B, benzene. Wavelengths in parentheses denote inflections, and those in double parentheses denote very indistinct inflections.

with the number of benzene rings in a molecule.

The conjugation band of *p*-phenylacetophenone is at an appreciably shorter wavelength than that of *p*-phenylbenzaldehyde, both the bands being structureless, (cf. Fig. 2). The conjugation bands of the two fluorenyl compounds have fine structures. Also with these compounds, the bands of the acetophenone analogue are at shorter wavelengths than the probably corresponding bands of the benzaldehyde analogue (cf. Fig. 3). These hypsochromic shifts of the conjugation bands observed in the comparison of the acetophenone analogues with the corresponding benzaldehyde analogues are considered to be mainly due to the steric effect of the methyl groups. This means that in these acetophenone analogues there exist steric interactions between the methyl groups and the benzene rings which cause the hypsochromic wavelength displacements of the conjugation bands relative to the conjugation bands of the corresponding benzaldehyde analogues, and that, consequently, the most probable configurations of these acetophenones are nonplanar.

By analogy with these facts, it may be inferred that the most probable configuration of acetophenone itself is nonplanar. Probably, the fact that the introduction of a methyl group at the carbonyl carbon atom of benzaldehyde to give acetophenone does not result in any appreciable hypsochromic wavelength displacement of the conjugation band is merely apparent. Further, this fact should not be considered to indicate the absence of the steric interference in acetophenone or the absence of the hypsochromic shift arising from the steric effect. It seems more reasonable to consider that the hypsochromic shift caused by the steric effect is so small that it is compensated by the electronic bathochromic effect of the methyl group. Accordingly, also the apparent absence of hypsochromic shift in *o*-methylated acetophenones, e. g. 2-methylacetophenone and 2, 4, 6-trimethylacetophenone, as compared with acetophenone should probably be interpreted similarly. From this point of view, not only the application of the hypothesis of Braude and others to the acetophenone derivatives but also their classification of steric effects in ultraviolet absorption spectra or their basic theory itself seems to be criticizable. This subject will be discussed more fully in the succeeding part of this series.

It remains to refer to the spectrum of 2-acetylfluorene in benzene shown in Fig. 4. It is of interest that this spectrum differs considerably from the spectrum in *n*-heptane. Thus, when

the solvent is changed from *n*-heptane to benzene, the first (from longer wavelengths side) maximum of fine structure of the conjugation band is reduced markedly in the intensity, and further, the second and the third maxima appear to merge into a maximum. Also with this compound, analogously to the cases of stilbene and related compounds discussed in earlier parts[11-13] of this series, considerably large red-shifts (about 3 mμ) associated with the change of solvent are observed.

Benzophenone

Lastly, the spectrum of benzophenone, which is shown in Fig. 1 and in Table I, is briefly discussed. It is evident that the two benzene rings in benzophenone can not be simultaneously coplanar with the plane of the carbonyl bond owing to the steric necessities. This situation is very similar to that in the case of 1, 1-diphenylethylene which will be treated in the succeeding part of this series. However, in contrast to the fact that 1, 1-diphenylethylene shows the conjugation band at almost the same position as the conjugation band of styrene, the conjugation band of benzophenone, which is structureless, has the maximum at an appreciably longer wavelength than that of benzaldehyde. This situation is rather similar to that observed in the comparison of the spectrum of tetraphenylethylene with that of *trans*-stilbene, the maximum of the former being at a longer wavelength than that of the latter[13]. Thus, it may be considered that the angle through which each benzene ring in benzophenone is rotated out of the plane of the carbonyl bond is not so large as the corresponding angle in 1, 1-diphenylethylene. However, it can not be asserted so, because the maximum of the conjugation band of benzophenone may be compared, alternatively, with the minor maximum of fine structure of the conjugation band of benzaldehyde at almost the same wavelength (i. e. at 248.1 mμ).

Experimental

All the spectra were measured with a Cary recording spectrophotometer Model 14 M-50.

The specimens of benzaldehyde and of acetophenone were obtained by distillation of commercial products under reduced pressure.

Benzophenone was prepared by the method described in Organic Syntheses[14]; colorless prisms melting at 48~48.5°C.

p-Phenylbenzaldehyde was prepared by the method described in Organic Reactions[15]. From 150 g. of biphenyl, 124 g. of the purified product was obtained after treatment with activated charcoal and repeated recrystallization from petroleum ether (b. p. 80~100°C); colorless thin plates melting at 60~61°C. About 5 g. of biphenyl was recovered.

p-Phenylacetophenone was prepared by the method described by Long and Henze[16]. From 77.1 g. of biphenyl, 87.4 g. of the purified product was obtained (89% of the theoretical amount); colorless crystals melting at 119~121.5°C.

2-Formylfluorene was prepared almost analogously to the preparation of *p*-phenylbenzaldehyde. Thus, a stream of dry carbon monoxide and hydrogen chloride was passed for about 4.5 hr. into a well-stirred solution of 42 g. of fluorene in 200 ml. of dry benzene containing 59 g. of anhydrous aluminum chloride and 11 g. of cuprous chloride at 35~40°C. The dark-colored reaction mixture was poured into a mixture of ice and small quantities of concentrated hydrochloric acid. The violet-colored mixture was extracted with benzene. The benzene solution was concentrated to about 300 ml. by evaporation, and the solution was shaken with an excess of a saturated solution of sodium bisulfite and small quantities of ethanol. The brown bisulfite compound was collected, washed repeatedly with ethanol and then with ether, and warmed with aqueous sodium carbonate. The aldehyde was then collected, dried on a porous plate, and crystallized twice from petroleum ether. The yield of faint yellow needles melting at 85.5~86.5°C was 6.3 g. It might be somewhat doubtful whether this product is the desired compound, 2-formylfluorene, because, according to Rodd[17], treatment of fluorene with ethyl formate and potassium ethoxide gives 9-formylfluorene which sinters at about 70°C and melts at about 90°C. However, the ultraviolet absorption spectrum of this product is considered to have revealed that this product is not 9-formylfluorene, but probably 2-formylfluorene.

2-Acetylfluorene was prepared by the method described in Organic Syntheses[18]. From 40 g. of fluorene, 24.4 g. of the product was obtained after purification by treatment with activated charcoal and by twofold recrystallization from ethanol (48.9% of the theoretical amount); colorless crystals melting at 127.5~128°C.

The author desires to thank Professor Kengo Shiomi for reading the manuscript and for valuable advice.

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14) H. Gilman (Editor-in-Chief), "Organic Syntheses", Col. Vol. I, John Wiley & Sons, Inc., New York (1932), p. 89.
15) R. Adams (Editor-in-Chief) "Organic Reactions", Vol. V, John Wiley & Sons, Inc., New York (1949), p. 298.
16) L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, 63, 1939 (1941).
17) E. H. Rodd, "Chemistry of Carbon Compounds", Vol. III B, Elsevier Publishing Co., Amsterdam (1956), p. 1454.
18) H. R. Snyder (Editor-in-Chief), "Organic Syntheses", Vol. 28, John Wiley & Sons, Inc., New York (1948), p. 3.

Relations between Electronic Absorption Spectra and Spatial Configurations of Conjugated Systems. XI. Styrene, 1, 1-Diphenylethylene and their Methylated Derivatives

By Hiroshi SUZUKI

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An introduction of a substituent into an *o*-, the α-, or the *cis*-β-position of styrene must cause a deviation of the phenyl group from the coplanar position with the plane of the ethylenic bond, owing to the steric interaction between the *o*-substituent and the α- or the *cis*-β-hydrogen or between the α- or *cis*-β-substituent and an *o*-hydrogen. On the other hand, in 1, 1-diphenylethylene, the two phenyl groups can not simultaneously be coplanar with the plane of the ethylenic bond. These steric situations must reveal themselves in the ultraviolet absorption spectra. In this part of the series, the method analogous to the one used so far in the previous parts of this series is applied to methylated styrenes, 1, 1-diphenylethylene, and its methylated derivatives, and the relations between the most probable spatial configurations of these compounds and the ultraviolet absorption spectra are discussed.

Calculation

The method of calculation is quite analogous to the ones for biphenyls[1], terphenyls[2], and stilbenes[3,4] in the earlier parts of this series. The $\pi-\pi$ resonance integral for the ethylenic bond is denoted by $\eta\beta$, and that for the $\alpha-1$ "single" bond of styrene is denoted by $\rho\beta$, in which β represents the $\pi-\pi$ resonance integral for a C–C bond in benzene as usual. By substituting suitable values for η and ρ according to the lengths and the angles of twist of the corresponding bonds, and by solving the secular equation for the determination of the molecular orbitals of styrene as linear combination of $2p\pi$ atomic orbitals by the usual procedure, the energy ΔE_A of the transition from the highest occupied orbital to the lowest vacant orbital, which is allowed by absorption of light polarized along the direction of the long axis of the molecule, is calculated. This value of ΔE_A is considered to correspond to the transition energy of the intense conjugation band of the molecule of the styrene-type of the configuration prescribed by the values of η and ρ.

The length of the ethylenic bond is assumed to be 1.34 Å, and hence the value of η is assumed to be 1.080 for the styrenes and 1, 1-diphenylethylenes throughout the present treatment, for the same reason as in the case of stilbenes in Part V[3] of this series. By using this value for η, the value of ΔE_A is calculated as a function of the variable ρ. The results are shown in Table I. It is seen in Table I that the value of ΔE_A increases with the decreasing value of ρ, and that the value of ΔE_A coincides with the value for benzene, $2(-\beta)$, when the value of ρ is zero.

TABLE I

ρ	1	0.9	0.8	0.7	0.6	
$\Delta E_A(-\beta)$	1.3958	1.4506	1.5082	1.5684	1.6314	
ρ	0.5	0.4	0.3	0.2	0.1	0
$\Delta E_A(-\beta)$	1.6968	1.7646	1.8342	1.9036	1.9672	2

Although reliable data concerning the spatial configuration of styrene molecule are not yet available, the configuration can be presumed by analogy with the following facts. Butadiene in the vapor phase has recently been found by Almenningen and his collaborators[5] to have probably almost exclusively the planar *trans*-configuration in which the length of the 2–3 "single" bond is 1.483±0.01 Å. On the other hand, biphenyl in the crystalline state has been found to have the planar configuration in which the length of the co-annular "single" bond is 1.48Å[6]. Accordingly, it may be presumed that styrene has probably the planar or nearly planar configuration in which the length of the $\alpha-1$ "single" bond is about 1.48 Å. Even if the presumption of the bond length is not correct, a small change in the bond length for the reference compound is considered not to affect significantly the resultant calculated values for

1) H. Suzuki, This Bulletin, **32**, 1340 (1959).
2) H. Suzuki, ibid., **33**, 109 (1960).
3) H. Suzuki, ibid., **33**, 379 (1960).
4) H. Suzuki, ibid., **33**, 410 (1960).
5) A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).
6) (a) J. Dhar, *Indian J. Phys.*, **7**, 43 (1932); *Chem. Abstr.*, **26**, 4517 (1932). (b) Idem., *Proc. Natl. Inst. Sci. India*, **15**, 11 (1949); *Chem. Abstr.*, **43**, 4655 (1949).

the angles of twist, as suggested by the results of the similar calculations for terphenyls in Part IV[2] of this series. Therefore, the presumption is adopted in the present treatment. Then, the relation between ρ and the angle of twist θ (i. e. the interplanar angle between the benzene ring and the ethylenic bond) as well as the length of the "single" bond R is assumed to be quite analogous to the relation between μ (the variable analogous to ρ) and θ as well as R postulated in the case of biphenyl in Part I[1] of this series. Thus, ρ is expressed as follows:

$$\rho = \cos\theta \times S(R, 0^\circ)/S(1.39, 0^\circ)$$
$$= \cos\theta \times 0.77108 + \cos^2\theta \times (1.54 - 1.48) \times 1.4458$$

where $S(R, 0^\circ)$ represents the $\pi-\pi$ overlap integral for the bond, the length and the angle of twist of which are R(Å) and 0°, respectively, and $S(1.39, 0^\circ)$ represents the overlap integral for a C-C bond in benzene, whose length is 1.39 Å and whose angle of twist is, of course, zero.

Accordingly, the value of ρ when R and θ are 1.48 Å and 0°, respectively, i. e. the value of ρ for the planar styrene molecule, is calculated to be 0.858, and the corresponding value of ΔE_A is calculated to be 1.475 $(-\beta)$, which is referred to as ΔE_L. When the wave number ν_A of the maximum of the conjugation band of a styrene derivative has been correlated with the calculated transition energy ΔE_A, the value of ρ for the compound can be evaluated, and then the corresponding values of θ and R can be estimated.

Styrenes

The data of the ultraviolet absorption spectra to be found in the literature for styrene and substituted styrenes are considerably variable. Especially the data of the molecular extinction coefficients are extremely variable, probably owing to the presence of polymeric materials in some of the specimens used, as pointed out already by Braude and Sondheimer[7]. Also with wavelengths of the absorption maxima, different workers using different instruments have reported values which vary by a few mμ. Further, the positions of the maxima vary more or less, depending on the solvent. With consideration for these situations, mainly the data obtained newly by the present author and those obtained recently by Schwartzman and Corson[8], both using Cary recording spectrophotometers and

TABLE II. ABSORPTION MAXIMA OF STYRENES

Styrene	Solvent			Conj. band				Ref.
		λ, mμ	ε	λ, mμ	ε	λ, mμ	ε	
Unsubstituted	C			248				8
p-Methyl-	C			253				8
trans-β-Methyl-	E	293	780	250	17300			9
		284	1100					
o-Methyl-	C			246				8
o,*p*-Dimethyl-	C			251				8
α-Methyl-	H	285.7	167	241.5	9780	215.4	8670	*a*
		278.1	311			200.0	20950	
α,β-Dimethyl-	E			244	8700			10
cis-β-Methyl-	E	290	120	240.6	13800			9
β,β-Dimethyl-	H	288.2	550	239.4	9060	(216)	8260	*a*
		280.3	800	(247.2)	6690			
		264.8	890					
o,*o'*-Dimethyl-	C			238				8
o,*p*,*o'*-Trimethyl-	O			245	7000			11
α,β,β-Trimethyl-	H	286.0	430	237.8	8440			*a*
		278.5	550	(245.3)	6210			
		275.5	550					
α,*o*-Dimethyl-	E	No max. between 210 and 300 mμ						12

Solvent: C, cyclohexane; E, ethanol; H, *n*-heptane; O, octane.
Wavelengths in parentheses denote inflections.
Ref. *a*, the present work.

7) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3773.
8) L. H. Schwartzman and B. B. Corson, *J. Am. Chem. Soc.*, **78**, 322 (1956).
9) R. Y. Mixer, R. F. Hech, S. Winstein and W. G. Young, ibid., **75**, 4094 (1953).
10) Y. Hirschberg, ibid., **71**, 3241 (1949).
11) K. C. Bryant, G. T. Kennedy and E. M. Tanner, *J. Chem. Soc.*, **1949**, 2389.
12) (a) M. J. Murray and W. S. Gallaway, *J. Am. Chem. Soc.*, **70**, 3867 (1948). (b) Ramart-Lucas and J. Hoch, *Bull. soc. chim. France*, [5] **5**, 848 (1938).

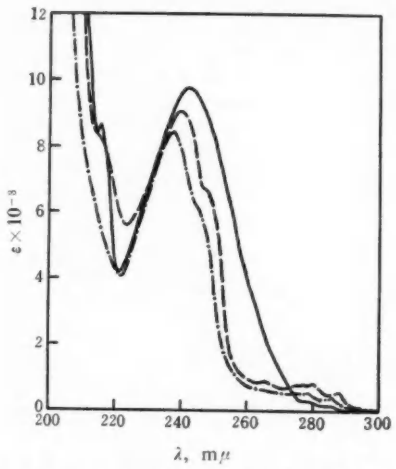

Fig. 1. Ultraviolet absorption spectra (in *n*-heptane): ——, α-methylstyrene; ----, β,β-dimethylstyrene; -·-·-, α,β,β-trimethylstyrene.

using saturated hydrocarbons as the solvents, are used in the present treatment. For a few compounds, the data of the spectra of which in solutions in saturated hydrocarbon are not available, the data for ethanol solutions are used. Such data used here are summarized in Table II, and the spectra measured by the present author are shown in Fig. 1.

It is evident that the styrene derivatives with methyl substituents in the sterically hindered positions exhibit the conjugation bands at shorter wavelengths than the conjugation band of the parent compound, styrene. The bands appearing in the range between 270 and 290 mμ are considered to be the ones corresponding to the $A_{1g}\rightarrow B_{2u}$ transition in benzene, quite similarly to the corresponding bands of benzaldehyde and of acetophenone[13].

In order to infer the spatial configurations of the styrenes from the data of the spectra by applying the above-mentioned calculation method, the electronic bathochromic effect of the methyl groups (probably due to the hyperconjugation effect) should be taken into account, because the wavelength separation between the conjugation band of styrene and the center of gravity of singlets of benzene as the shorter-wavelength-side reference is so small that the magnitude of the bathochromic effect of the methyl groups may not be negligible relatively to the magnitude of the steric hypsochromic effect.

The allowance for the electronic bathochromic effect of the methyl groups is made by the method analogous to the ones used in the treatments of *o*-alkylbiphenyls in Part II[14] of this series and of the stilbene derivatives with methyl groups on the benzene nuclei in Part VIII[15] of this series, i. e. by choosing pertinently the longer-wavelength-side and the shorter-wavelength-side references in the correlation of ν_A with ΔE_A.

Longer-wavelength-side Reference. — As the value of ν_A corresponding to ΔE_L, viz. ν_L, the wave number, at which the molecule concerned would exhibit the absorption maximum of the conjugation band if the molecule were planar, is taken. Thus, for example, as the value of ν_L for *o*-methylstyrene, the wave number of the absorption maximum of the conjugation band of *p*-methylstyrene, 39526 cm^{-1} (253 mμ), is taken, since the electronic bathochromic effect of a methyl group can be considered to be approximately equivalent in the *o*- and *p*-positions.

From the comparison of the spectrum of *p*-methylstyrene with that of styrene and the comparison of the spectrum of *o*,*p*-dimethylstyrene with that of *o*-methylstyrene, it may be presumed that the magnitude of the bathochromic displacement of the conjugation band per a methyl substituent at the *p*- or *o*-position of styrene is about 5 mμ. Further, it may be assumed that the displacement is approximately additive, on the analogy of the case of methylated benzenes[16]. According to Schwartzman and Corson[8], *m*-methylstyrene and *m*,*m*'-dimethylstyrene in cyclohexane solutions exhibit the conjugation bands at 251 and 254 mμ, respectively. Comparing these wavelengths with that of styrene itself (248 mμ), it is seen that the magnitude of the bathochromic displacement per a methyl group at a *m*-position is 3 mμ, and that the additivity holds good in this case. The magnitude of the bathochromic displacement caused by an *o*-methyl group may, strictly speaking, be not completely equal to that by a *p*-methyl group. Probably, the former is very slightly smaller than the latter, in view of the results of the calculations for *p*- and *o*-terphenyls described in Part IV[2] of this series, but must be considerably larger than the magnitude of the bathochromic displacement caused by a *m*-methyl group. Therefore, the assumption that the magnitude of the displacement per an *o*-methyl group is equal to that per a *p*-methyl group can be considered to be quite satisfactory in the present approximate treatment. When it is assumed so, *o*,*p*-dimethylstyrene would have the absorption maximum of the conjugation band at about 258 mμ (248+5×2 mμ) if it were not for

13) H. Suzuki, This Bulletin, 33, 613 (1960).

14) H. Suzuki, ibid., 32, 1350 (1959).
15) H. Suzuki, ibid., 33, 406 (1960).
16) K. F. Herzfeld, *Chem. Revs.*, 41, 233 (1947).

TABLE III. RESULTS OF CALCULATION FOR STYRENES

Group	Entry No.	Styrene	λ_A mμ	λ_L mμ	λ_S mμ	ΔE_A $-\beta$	ρ	$\theta°$	R Å
I	1	Unsubstituted	248			1.475	0.858	0	1.48
	2	*p*-Methyl-	253					0	
	3	*trans*-β-Methyl-	250					0	
II	4	*o*-Methyl-	246	253	213.3	1.555	0.722	31	1.489
	5	*o,p*-Dimethyl-	251	258	217.3	1.553	0.725	30.7	1.489
	6	α-Methyl-	241.5	250	208.3	1.567	0.702	33	1.490
	7	α,β-Dimethyl-	244	252	208.3	1.557	0.719	31.5	1.489
III	8	*cis*-β-Methyl-	240.6	250	208.3	1.578	0.685	35.2	1.491
	9	β,β-Dimethyl-	239.4	252	208.3	1.607	0.639	40	1.494
IV	10	*o,o'*-Dimethyl-	238	258	217.3	1.711	0.480	54	1.505
	11	*o,p,o'*-Trimethyl-	245	263	219.3	1.669	0.543	49	1.500
	12	α,β,β-Trimethyl-	237.8	254	208.3	1.638	0.590	45	1.498
V	13	α,*o*-Dimethyl-						(90)	

the steric hypsochromic effect. Accordingly, for the treatment of *o,p*-dimethylstyrene, the value of 38760 cm^{-1} (258 mμ) is taken as the value of ν_L.

Further, for example, for *cis*-β-methylstyrene, the wave number of the maximum of *trans*-β-methylstyrene is taken as ν_L. The magnitude of the bathochromic wavelength displacement caused by the introduction of a methyl group into the α-position and that by the introduction into a β-position may be not equal to each other, since the two positions must be not equivalent, the α-methyl group being at the position of cross-conjugation to the conjugated system of the styrene skeleton and, on the other hand, the β-methyl group being at the position of conjugation to the conjugated system. In spite of this, the magnitude of the displacement by an α-methyl as well as a β-methyl group is provisionally assumed to be equal to the difference in wavelength between the maximum of *trans*-β-methylstyrene and that of styrene, 2 mμ, although the data of the maxima of these compounds may be not pertinent to comparison, since they are obtained in different solvents. Further, it is assumed that the additivity holds good also in this case. Then, for example, the value of ν_L for the treatment of α, β, β-trimethylstyrene becomes 39370 cm^{-1} (254 mμ = 248 + 2 × 3 mμ).

Shorter-wavelength-side Reference.—The value of ΔE_A when ρ is zero, $2(-\beta)$, is denoted by ΔE_S, and the corresponding wave number is denoted by ν_S, as usual. As the value of ν_S for the treatments of the styrenes which have no methyl substituent on the benzene nuclei, the center of gravity of singlets of benzene, 48000 cm^{-1} (208.3 mμ), is taken, as usual.

As shown in Table II in Part II[14] of this series, the absorption bands of toluene, *m*-xylene, and mesitylene are at longer wavelengths by about 5, 9 and 11 mμ, respectively, than the corresponding bands of benzene. Accordingly, the values for these compounds corresponding to the center of gravity of singlets of benzene are considered to be approximately 46882 cm^{-1} (213.3 mμ = 208.3 + 5 mμ), 46019 cm^{-1} (217.3 mμ = 208.3 + 9 mμ), and 45600 cm^{-1} (219.3 mμ = 208.3 + 11 mμ), respectively. Therefore, for example, as the value of ν_S for the treatment of *o, p, o'*-trimethylstyrene, the value of 45600 cm^{-1} is taken.

Application of the Calculation. — When the references have been determined for each styrene derivative as mentioned above, the value of the calculated transition energy ΔE_A corresponding to the observed position (ν_A in wave number) of the maximum of the conjugation band of the compound can be easily obtained by the use of the usual postulated linear relation of ΔE_A to ν_A between the two reference points. Consequently, from the value of ΔE_A, the corresponding value of ρ can be obtained according to the relation between ρ and ΔE_A shown in Table I, and then the corresponding values of θ and R can be obtained. The results of the calculations are shown in Table III, in which λ_A refers to the wavelength of the absorption maximum of the compound concerned, and λ_L and λ_S refer to the corresponding longer-wavelength-side and the corresponding shorter-wavelength-side references, respectively, in wavelength.

Discussion

Although much reliance may not be placed on the individual numerical values of the calculated interplanar angles because of the approximation used, the results of the calculations shown in Table III appear to lead to the

conclusion that these styrenes can be classified into the following well-defined groups with respect to the type or the degree of the steric interaction involved in the molecule.

Group I. The compounds which have no methyl substituent at hindering positions, i.e. at *o*-, α-, and *cis*-β-positions. To this group, the compounds of the entry numbers 1—3 listed in Table III belong. These compounds are probably planar.

Group II. The compounds which have one hindering methyl group either at an *o*-position or at the α-position of the molecule. These compounds are considered to involve solely the steric interference either between the *o*-methyl group and the α-hydrogen or between the α-methyl group and an *o*-hydrogen. To this group, the compounds of the entry numbers 4–7 in Table III belong. The β-methyl group in "α, β-dimethylstyrene" (entry 7) is probably *trans* to the phenyl group. The calculated interplanar angles for these compounds range from 31° to 33°.

Group III. The compounds with one hindering methyl group at the *cis*-β-position. These compounds involve solely the steric interference between the *cis*-β-methyl group and an *o*-hydrogen. To this group, the compounds of the entry numbers 8 and 9 belong. For these compounds, the calculated interplanar angles are 35° and 40°, being slightly larger than those for the compounds belonging to Group II.

Group IV. The compounds with two hindering methyl groups either at both *o*-positions or at the α- and the *cis*-β-positions. These compounds involve the steric interferences between methyl groups and hydrogen atoms on both the sides of the benzene nucleus. To this group, the compounds of the entry numbers 10–12 in Table III belong. The calculated interplanar angles for these compounds range from 45° to 54°, and are considerably larger than those for the compounds belonging to Group II and those for the compounds belonging to Group III.

Group V. To this group, α, *o*-dimethylstyrene (entry 13) belongs. If the most probable configuration of this compound were the configuration involving the steric interference between the α-methyl group and the *o*-hydrogen and the interference between the *o*-methyl group and the *cis*-β-hydrogen, this compound would belong to Group IV and not to Group V. In fact, however, this compound has been reported to show no absorption maximum in the range between 210 and 300 mμ, in contrast with the compounds belonging to Group IV. Accordingly, the most probable configuration of this compound is probably the one in which the two methyl groups just contact with each other, and consequently, the interplanar angle is larger than in the compounds belonging to Group IV and probably nearly 90°. This inference seems to be not unlikely, in view of the fact that *o*, *o*'-dimethylbiphenyl has probably the *cis*-like configuration in which the two methyl groups contact with each other as discussed in Part II[14] of this series.

The fact that the calculated interplanar angles for the compounds belonging to Group III are appreciably larger than those for the compounds belonging to Group II is of interest. This fact seems to lead to the conclusion that the steric interference due to the *cis*-β-methyl group is more effective than that due to the α-methyl group.

The geometries of the relevant parts of the compounds belonging to Group IV are considered to be approximately similar to those of *trans*-α, α'-dimethylstilbene and of *trans*-2, 4, 6, 2', 4', 6'-hexamethylstilbene, except for the possible differences of the bond lengths and of the bond angles. The calculated interplanar angle for α, β, β-trimethylstyrene (entry 12) is considerably smaller than that for *trans*-α, α'-dimethylstilbene (58°)[17]. On the other hand, the calculated interplanar angle for *o*, *o*'-dimethylstyrene (entry 10) coincides almost completely with that for *trans*-hexamethylstilbene (54.3°)[15].

At any rate, it is noteworthy that the interplanar angles for the compounds which involve the steric interferences between methyl groups and hydrogen atoms on both sides of the benzene ring (belonging to Group IV) are considerably larger than those for the compounds which involve the steric interference solely on one side of the benzene ring (belonging either to Group II or to Group III). This may mean that in the compounds with the steric interference solely on one side of the benzene ring the steric interference is relieved to some extent probably by changes in the bond angles.

Lastly in this section, it may be concluded that, by making allowance for the electronic bathochromic effect of the methyl substituents, the interplanar angles in the methylated styrenes have been almost satisfactorily inferred from the wavelength positions of the conjugation bands.

Criticism on Braude and Forbes' Classification of Steric Effects in Ultraviolet Absorption Spectra

Braude and his coworker[18] classified the steric effects of twisting of "single" bonds in conjugated systems on the conjugation bands into

17) H. Suzuki, This Bulletin, 33, 396 (1960).
18) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 1955, 3754.

two types: (1) Steric effect which gives rise to intensity changes only, without causing any "unusual" change in wavelength (the steric effect of type 1, or *type 1* steric effect). This effect is caused by relatively small twists. (2) Steric effect which causes changes in both wavelength and intensity (the steric effect of type 2, or *type 2* steric effect). This effect is caused by larger twists than the first effect.

To the above two types, Forbes[19] has recently added a third type; the steric effect occurring when the twist is so large that conjugation across the bond is almost completely inhibited and the molecule absorbs as two distinct entities. This effect has been termed a *type 3* steric effect.

A similar classification of steric effects into three main classes has been proposed also by Turner and Voitle[20], and such a classification appears to have been generally accepted[21].

Braude and Sondheimer have regarded *o*-methylated styrenes and related compounds[7] as well as *o*-methylated benzaldehydes and acetophenones[18] as examples of the compounds exhibiting the steric effect of type 1, and have applied their postulated equation $\cos^2\theta = \varepsilon/\varepsilon_0$ to these compounds, where ε and ε_0 are the molecular extinction coefficient of the conjugation band of a given compound and that of the corresponding planar reference compound, respectively. According to the results, the estimated interplanar angles between the phenyl group and the CH=CX group in styrenes and related compounds are about 20~30° for one, and about 40~60° for two *o*-methyl substituted compounds.

On the other hand, Braude and Forbes[22] have stated that *o*-methylbiphenyl provides an excellent example of the steric effect of type 2, in contrast with *o*-methylated styrenes and acetophenones, notwithstanding the fact that the geometries of the relevant parts of these systems are quite similar. They have explained this rather strange difference between the biphenyl system on the one hand, and the acetophenone and styrene systems on the other, as follows: "the two possible uniplanar conformations of this compound (*o*-methylbiphenyl) are identical and involve the same extent of steric hindrance, whereas the two uniplanar conformations of 2-methylacetophenone or 2-methylstyrene are not identical and one involves much less steric hindrance than the other. Hence the steric hindrance produced by an *o*-methyl substituent will be effectively much larger in the biphenyl than in the other two systems, and the probability of any *o*-substituted biphenyl molecule's occupying a near-planar vibrational state will be extremely low. Thus, the conditions prerequisite for the display of steric effects of type 1 no longer exist".

This appears to be their main reason, although they have given two additional reasons. If this explanation were acceptable, why do *o,o'*-dimethyl substituted styrenes and acetophenones, e. g. 2, 4, 6-trimethylstyrene, 2, 6-dimethylbenzylideneacetone, and 2, 6-dimethylacetophenone, belong to the group of compounds which exhibit the steric effect of type 1 as Braude and his coworker have stated?

It will be evident, as seen in the present treatment of the styrenes and as discussed for the case of acetophenones in the preceding part[13] of this series, that the electronic bathochromic effect of the substituents is responsible for the apparent absence of an appreciable hypsochromic displacement of the conjugation band in these compounds. That is, it seems that the apparent absence of an appreciable wavelength displacement is not a proof of the absence of the hypsochromic displacement produced by the steric interaction but should be considered as a result of compensation of the hypsochromic effect by the electronic bathochromic effect of the substituents. The apparent bathochromic displacement observed sometimes with hindered compounds should, of course, be considered to be due to the electronic bathochromic effect of the substituents outweighing the steric hypsochromic effect. These considerations imply that the difference between the steric effect of type 1 and the steric effect of type 2 is not the difference in kind or in underlying mechanism as Braude and Forbes have asserted, but merely in degree.

In general, as has been discussed so far in this series, the electronic transition energy and hence the wavelength at which absorption occurs are determined by the spatial configuration or conformation of the molecule. Thus, so far as the conformation about the "single" bond is concerned, the non-planarity of the conformation must in principle produce a more or less large hypsochromic shift of the conjugation band, depending on the degree of the deviation from the coplanarity. On the other hand, the presence of steric interference in the molecule affects invariably the population ratio among conformations, and changes the most probable conformation from the planar conformation to a nonplanar one in most cases. Therefore, the wavelength displacement of the

19) W. F. Forbes, "Steric Effects in Conjugated Systems", edited by G. W. Gray, (Proceedings of a Symposium held at the University, Hull, 15-17 July, 1958 by the Chemical Society), Butterworths Scientific Publications, London (1958), p. 62.
20) R. B. Turner and D. M. Voitle, *J. Am. Chem. Soc.*, 73, 1403 (1951).
21) M. S. Newman (ed.), "Steric Effects in Organic Chemistry", John Wiley & Sons, Inc., New York (1956), p. 484.
22) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1955, 3776.

conjugation band caused by steric interference is not an unusual phenomenon as Braude and others have stated, but rather a usual one.

Either when the steric interference is so weak that the planar or nearly planar conformation is still the most probable one, or when the transition probability in the more probable nonplanar conformation is much smaller than the transition probability in the less probable planar conformation, it might be possible that the absorption maximum in the resultant spectrum of the sterically hindered compound is at the same wavelength as the maximum of the unhindered planar reference compound, the intensity of the former being smaller than that of the latter. However, it is doubtful whether such cases can exist in fact. The so-called steric effect of type 1 is, as mentioned above, merely superficial or spurious with respect to the steric effect, and should be considered as a special case where the steric hypsochromic shift is so small that it is almost completely compensated by the bathochromic shift due to the electronic effect of the substituents. Further, only considering that, as pointed out already in an earlier part[23] of this series, the hypsochromic shifts of the conjugation bands as compared with the bands of the corresponding planar reference compounds are observed even in the spectra cited by Braude and others as examples of the steric effect of type 1, it will be evident that the effect of this type is not clear-cut even phenomenologically.

Attention to the fact that, even when any significant wavelength displacement is apparently not observed, the presence of steric interference in the molecule or the deviation of the most probable molecular configuration from the coplanarity can manifest itself in a decrease in the intensity of the band may be of some practical significance, whatever the underlying mechanism may be. It seems, however, not to be necessary in principle to consider the so-called steric effect of type 1 separately from the so-called steric effect of type 2. Further, the steric effect of type 3 (i. e. the *type 3* steric effect) is merely the extreme case of the steric effect of type 2. Accordingly, it may be concluded that Braude and Forbes' classification of steric effects and their elucidations of the "mechanisms underlying the different types" are quite redundant, as pointed out also by Dewar[24].

1, 1-Diphenylethylenes

In 1, 1-diphenylethylene, the two phenyl groups can not be simultaneously coplanar with the ethylenic bond, owing to the steric necessities. Therefore, the most probable configuration of this molecule is presumed to be the configuration in which both of the phenyl groups are rotated out to the same extent as each other from the plane of the ethylenic bond, or alternatively, the configuration in which one of the phenyl groups is almost perpendicularly rotated out of the plane of the ethylenic bond, leaving the other phenyl group coplanar with the ethylenic bond.

The data of the ultraviolet absorption spectra of 1, 1-diphenylethylene and its methylated derivatives are summarized in Table IV, in which the data of the spectrum of styrene are also included for comparison. In addition, the spectra of 1, 1-diphenylethylene and its 2, 2-dimethyl derivative measured by the present author are shown in Fig. 2. These spectra are similar to each other, except for the appearance of the additional band at 235.4 mμ besides the principal band at 248.0 mμ in the spectrum of 1, 1-diphenylethylene. It is especially of interest that the absorption maxima of the principal (conjugation) bands of these four compounds appear at the almost identical wavelength.

The close similarity between the spectrum of 1, 1-diphenylethylene and that of styrene would be considered as supporting the second of the two hypotheses mentioned above concerning the

Table IV. Absorption maxima of 1, 1-diphenylethylenes

1, 1-Diphenylethylene	Solvent			Conjugation band		Ref.
		λ, mμ	ε	λ, mμ	ε	
Unsubstituted	H			248.0	14270	*a*
				235.4	13730	
2-Methyl-				ca. 248	ca. 13000	25
2, 2-Dimethyl-	H	(286.5)	1320	248.0	11700	*a*
		(279.0)	1900			
(Styrene)	C			248		8

Solvent: H, *n*-heptane; C, cyclohexane. Wavelengths in parentheses denote inflections.
Ref. *a*, the present work.

23) H. Suzuki, This Bulletin, 32, 1357 (1959).
24) M. J. S. Dewar, Ref. 19, p. 71.
25) Ramart-Lucas and P. Amagat, *Bull. soc. chim. France*, [4] 51, 108 (1932).

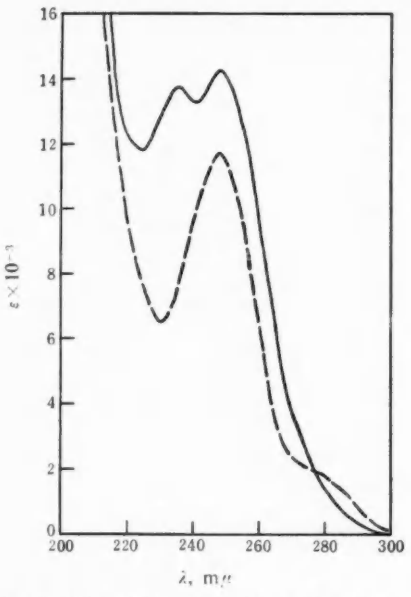

Fig. 2. Ultraviolet absorption spectra (in *n*-heptane): ——, 1, 1-diphenylethylene; ----, 1, 1-diphenyl-2, 2-dimethylethylene.

most probable configuration of 1, 1-diphenylethylene. However, the close similarity between the spectrum of 1, 1-diphenylethylene and the spectra of its methylated derivatives seems to suggest that the first hypothesis is more plausible, because especially the dimethyl derivative (1, 1-diphenyl-2-methylpropene) can not assume the configuration of the second hypothesis owing to the steric interferences between the phenyl groups and the methyl groups at the *cis*-β-positions relative to the phenyl groups.

Now, when it is assumed that 1, 1-diphenylethylene as well as its derivatives has the configuration in which a styrene chromophore is left as the second hypothesis, these compounds can be treated by the calculation quite similar to the one in the case of styrenes.

Alternatively, when it is assumed that each compound has a configuration in which the two phenyl groups are rotated out by the identical degree from the plane of the ethylenic bond as the first hypothesis, the secular equation for the determination of the molecular orbitals as linear combinations of the $2p\pi$ atomic orbitals can be factorized into one equation identical in the form with the one for styrene and one equation for benzene, when ρ' is $1/\sqrt{2} \times \rho$, $\rho'\beta$ representing the $\pi - \pi$ resonance integral for each bond connecting a phenyl group to an ethylenic carbon atom. This situation is very similar to that in the treatment of tetraphenylethylene in Part VI[26] of this series. Accordingly, also in this case, the calculation similar to the one for styrenes can be applied to these 1, 1-diphenylethylenes, and from the values of ρ obtained as results of the calculation, the values of ρ' can be obtained. Then, from the values of ρ', the values of θ and R can be obtained by the use of the relation quite analogous to the one between ρ and θ as well as R postulated already. The results of the calculation are shown in Table V, in which the symbols have the same significance as in Table III. Allowance for the electronic bathochromic effect of methyl groups has been made by the method quite analogous to the one used in the case of the styrenes. In 1, 1-diphenyl-2-methylethylene, the positions of the two phenyl groups are not completely equivalent, and therefore, their angles of twist θ must differ, though probably very slightly, from each other. In spite of this, the results for this compound obtained on the basis of the assumption that the angles of twist of the two phenyl groups are equal are shown.

It is noteworthy that the introduction of methyl groups into the 2- or β-positions of 1, 1-diphenylethylene affects only slightly the calculated interplanar angle θ. The presence of the additional steric interference by the methyl groups in spite of the apparent absence of a wavelength displacement of the conjugation band is evident from the fact that the intensity of the band is decreased in the order 1, 1-diphenylethylene > 1, 1-diphenyl-2-methylethylene > 1, 1-diphenyl-2, 2-dimethylethylene, with the increasing number of methyl substituents. Thus, also in this case, the apparent absence of a wavelength displacement of the conjugation band is considered as the result of the compensation of the hypsochromic shift due to the steric interference by the bathochromic shift due to the electronic (probably hyperconjugation) effect of the methyl groups. Lastly, it may be mentioned that the calculated interplanar angles for these compounds, especially for the dimethyl compound, are very similar to those for the styrene derivatives belonging to Group IV (cf. Table III).

Exaltation of Molecular Refraction

Mulliken[27] has indicated that the molecular refractions of positional isomeric alkylstyrenes should roughly parallel the ultraviolet absorption maxima. Following this view, Schwartzman and Corson[2] have correlated the ultraviolet absorption spectra of styrene derivatives with methyl substituents on the benzene nucleus with the molecular refractions. The present author also has frequently referred so far in this series to

26) H. Suzuki, This Bulletin, 33, 389 (1960).
27) R. S. Mulliken, *J. Chem. Phys.*, 7, 356 (1939).

TABLE V. RESULTS OF CALCULATION FOR 1,1-DIPHENYLETHYLENES

1,1-Diphenylethylene	λ_A mμ	λ_L mμ	λ_S mμ	ΔE_A $-\beta$	ρ	ρ'	$\theta°$	R Å
Unsubstituted	248	248	208.3	1.475	0.858	0.607	43.5	1.496
2-Methyl-	248	250	208.3	1.496	0.821	0.581	46	1.498
2,2-Dimethyl-	248	252	208.3	1.515	0.788	0.557	48	1.500

TABLE VI

Compound	EM_α	EM_D	$E\Sigma_\alpha$	$E\Sigma_D$	Ref.
Styrene					
Unsubstituted		1.37			9
		1.10		0.97	28
			1.10	1.13	29
			1.05	1.10	30
p-Methyl-			1.40	1.48	29
trans-β-Methyl-		1.87			9
			1.09	1.19	30
α-Methyl-		0.94			9
		0.64		0.55	28
			0.62	0.68	29, 30
α,β-Dimethyl-		0.70			9
			0.63	0.67	29, 30
cis-β-Methyl-		1.00			9
β,β-Dimethyl-			0.64	0.70	29, 30
α,β,β-Trimethyl-		0.59			9
		0.50		0.34	28
			0.44	0.48	30
1,1-Diphenylethylene					
Unsubstituted			0.88	0.95	30
2-Methyl-	1.86	2.10	0.96	1.08	30
2,2-Dimethyl-	1.39	1.53	0.67	0.74	30

EM_α and EM_D are exaltations of molecular refraction.
$E\Sigma_\alpha$ and $E\Sigma_D$ are specific exaltations.

the exaltation of the molecular refraction as a measure of the degree of conjugation.

In Table VI, the data of the exaltations found in the literature for the styrenes and the 1,1-diphenylethylenes treated in this part of the series are summarized. The data for some compounds are considerably variable, depending on the worker. In addition, the values of the exaltations are considered to contain not only the conjugation effect but also the hyperconjugation effect of the methyl groups. Therefore, it may not be pertinent to correlate these values of the exaltations directly with the calculated interplanar angles or with the degrees of conjugation which will be inferred from the calculated interplanar angles. Notwithstanding, it will be seen that there exist roughly regular relations among these quantities.

Experimental

All the spectra were measured with a Cary recording spectrophotometer Model 14 M-50.

α-Methylstyrene (2-phenylpropene) was prepared after the procedure described by Klages[31], and purified by repeated distillation; colorless liquid, b. p. 160~162°C. The value of boiling point is in good agreement with those found in the literature (162°C[31], 160~162°C[32]).

β,β-Dimethylstyrene (1-phenyl-2-methylpropene) was prepared, after the procedure described by Tiffeneau[33], by dehydration of 1-phenyl-2-methylpropanol by heating with oxalic acid, and was purified by repeated distillation; colorless liquid, b. p. 189~193°C. The boiling point of this compound found in the literature is 179~189°C[33]. 1-Phenyl-2-methylpropanol was prepared by the Grignard reaction of benzaldehyde and the Grignard reagent prepared from isopropyl bromide and magnesium.

α,β,β-Trimethylstyrene (2-phenyl-3-methyl-2-butene) was prepared by dehydration of 2-phenyl-3-methyl-2-butanol by distillation, and purified by repeated distillation; colorless liquid, b. p. 189~

28) K. v. Auwers and F. Eisenlohr, *Ber.*, **43**, 806 (1910).
29) K. v. Auwers, ibid., **45**, 2781 (1912).
30) K. v. Auwers, ibid., **62**, 693 (1929).
31) L. Klages, ibid., **35**, 2640 (1902).
32) M. Tiffeneau, *Compt. rend.*, **134**, 845 (1902).
33) M. Tiffeneau, *Ann. Chim.*, [8] **10**, 365 (1907).

191°C. The value of boiling point is in good agreement with the value found in the literature. 2-Phenyl-3-methyl-2-butanol was prepared by the Grignard reaction from acetophenone and isopropyl bromide.

The specimen of 1,1-diphenylethylene used was obtained by re-distillation under reduced pressure of the material prepared by Dr. Takahasi in this laboratory by the method described in Organic Syntheses[34]; colorless thin plates; b. p. 140~143°C/16 mmHg.

1,1-Diphenyl-2,2-dimethylethylene (1,1-diphenyl-2-methylpropene) was prepared by dehydration of 1,1-diphenyl-2-methylpropanol by refluxing with a few pieces of biscuit chips impregnated with concentrated sulfuric acid, and purified by distillation; colorless liquid, b. p. 167~169°C/22 mmHg. The value of boiling point of this compound found in the literature is 150~152°C/15 mmHg[35] and 280~282°C/775 mmHg[36]. 1,1-Diphenyl-2-methylpropanol was prepared by the Grignard reaction from benzophenone and isopropyl bromide.

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34) H. Gilman (Editor-in-Chief), "Organic Syntheses", Col. Vol. 1, John Wiley & Sons, Inc., New York (1932), p. 221.

35) Ramart-Lucas and M. E. Salmon-Legagneur, *Bull. soc. chim. France*, [4] **45**, 728 (1929).

36) J. Levy, ibid., [4] **29**, 882 (1921).

Reaction of Troponoids and Organometallic Compounds. V. Reaction of Bromotropolones and Alkylmagnesium Iodides

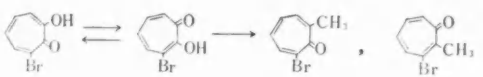
By Katsuo KIKUCHI

(Received October 19, 1959)

It has been reported in a previous paper[1] of this series that bromo derivatives of tropolone methyl ether react with α- and β-naphthylmagnesium bromides to yield corresponding bromo substitution products of 2-α- and 2-β-naphthyltropones and 2-hydroxyphenyl α- and β-naphthyl ketones.

The present paper deals with an investigation on the reaction of bromotropolones and alkyl Grignard reagents.

Reaction of methylmagnesium iodide and 3-bromotropolone (Ia) yielded colorless plates (IIa) whose ultraviolet spectrum was similar to that of tropone[2] (Fig. 1), suggesting that it is monobromo-2-methyltropone. As 3-bromotropolone is in a "high mobile tautomeric" system as represented with A and A′, two isomeric monobromo-2-methyltropone, i.e. 7-bromo-2-methyltropone (B) and 3-bromo-2-methyltropone (B′) should be obtained by this reaction. Actually, treatment of IIa with dilute alkali gave *o*-toluic acid (IIIa) indicating that IIa is 7-bromo-2-methyltropone (B).



A A′ B B′

However, the reaction of 3,7-dibromotropolone and methylmagnesium iodide under similar condition gave only minute amount of unidentified phenolic substance. Similarly, the reaction of 3,5,7-tribromotropolone and methylmagnesium iodide afforded only a small amount of dimethyl 3,5-dibromo-2-hydroxyphenyl carbinol which was proved to be identical with that synthesized by the reaction of methyl 3,5-dibromosalicylate and methylmagnesium iodide.

On the other hand, by the reaction of 3,7-dibromotropolone methyl ether (Ib) and methylmagnesium iodide 3,7-dibromo-2-methyltropone (IIb) was obtained. By treatment with alkali IIb was submitted to rearrangement to give 3-bromo-*o*-toluic acid (IIIb)[3], debromination of which gave IIIa. The ultraviolet absorption spectrum of IIb (Fig. 1) showed bands characteristic of tropone.

1) Part IV: K. Kikuchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 505 (1960).

2) T. Nozoe, T. Mukai and K. Takase, *Sci. Repts. Tohoku Univ., Ser.* I, **39**, 164 (1956).

3) D. Peltier, *Compt. rend.*, **237**, 357 (1954).

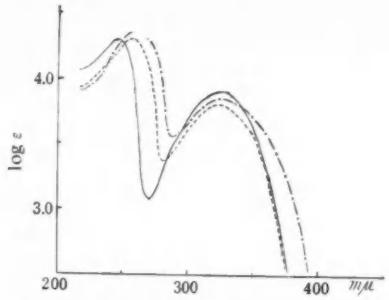
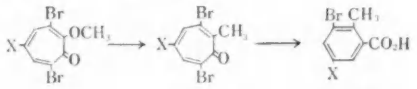


Fig. 1. Ultraviolet absorption spectra of IIa (——), IIb (------) and IIc (—·—·—) in methanol.

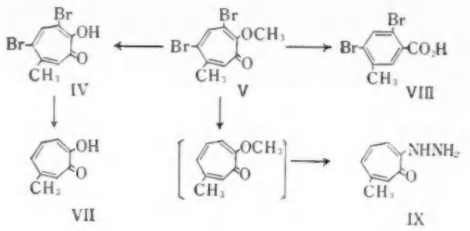
Reaction of 3, 5, 7-tribromotropolone methyl ether (Ic) and methylmagnesium iodide afforded four kinds of crystals as follows: pale yellow prisms (IIc), m. p. 63~64°C; colorless needles (IV), m. p. 151.5~153°C; colorless needles (V), m. p. 151~152°C and colorless needles (VI), m. p. 116~117°C. The main product was IIc.

Treatment of IIc with alkali afforded an acid (IIIc) whose debromination gave *o*-toluic acid (IIIa). This fact and the analytical values of IIc and IIIc indicate that IIc and IIIc are 2-methyl-3, 5, 7-tribromotropone and 3, 5-dibromo-*o*-toluic acid, respectively. The ultraviolet spectrum of IIc is shown in Fig 1.



Ib,Ic IIb,IIc IIIb,IIIc

IV showed red coloration with ferric chloride characteristic of tropolone and gave yellow sodium salt with aqueous sodium carbonate. On catalytic debromination, IV afforded 4-methyltropolone (VII)[4,5]. Treatment of V with hydrobromic acid in aqueous acetic acid and with aqueous sodium hydroxide afforded IV and 4, 6-dibromo-*m*-toluic acid (VIII)[6], respectively. Catalytic debromination of V on palladium-charcoal gave colorless crystals which, on treatment with hydrazine hydrate, was converted to 2-hydrazino-6-methyltropone (IX)[7]. These experimental results indicate that IV is 3, 5-dibromo-6-methyltropolone and V is 3, 5-dibromo-2-methoxy-6-methyltropone as shown in the following scheme.



IV V VIII

VII IX

It was reported previously that the reaction of 7-bromo-2-methoxytropone and phenylmagnesium bromide afforded phenyltropolone[8], m. p. 96~97°C, as a by-product. Pauson[9] suggested it to be 4-phenyltropolone and later Kitahara[10] presented the mechanism of its formation. The formation of IV and V also could be explained by his mechanism.

Analysis of VI is in agreement with the formula $C_9H_8OBr_2$ and its ultraviolet absorption spectrum (Fig. 2) is quite similar to those of IIa—IIc, and it is suggested that VI has a tropone nucleus. Presumably VI will be 3, 5-dibromo-2, 7-dimethyltropone or 3, 5-dibromo-2, 6-dimethyltropone formed either by the reaction of excess of methylmagnesium iodide with IIc or V, but the determination of the structure was impossible because of limited amount of the material.

Application of ethylmagnesium iodide to Ib afforded 3, 7-dibromo-2-ethyltropone (IId), as in the case of IIb. IId was converted to 3-bromo-2-ethylbenzoic acid (IIId), and the latter was debrominated to 2-ethylbenzoic acid (IIIe). The same reaction of ethylmagnesium iodide with Ic gave no crystalline product even after chromatographic separation on an alumina column. Ethanolic solution of the oil thereby obtained, however, when treated with dilute alkali, resulted in the formation of dibromo-2-ethylbenzoic acid (IIIf) and its ethyl ester (IIIg). From this fact it seems reasonable to assume that 2-ethyl-3, 5, 7-tribromotropone (IIe) was formed in this reaction as in the case of IIc.

Some nucleophilic reactions on IIa, IIb and IIc were next examined.

Heating of IIa and IIb with *p*-toluidine respectively afforded 2-methyl-7-(*p*-toluidino)-tropone (Xa) as yellow prisms and 3-bromo-2-methyl-7-(*p*-toluidino)-tropone (Xb) as yellow plates. The ultraviolet spectrum of Xa was shown in Fig. 2. Similarly, heating of IIa and IIb with aniline respectively gave 7-anilino-2-methyltropone (Xc) as an oil and 7-anilino-3-bromo-2-methyltropone (Xd) as yellow crystals.

Application of hydrazine hydrate to IIa at

4) R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, **1948**, 1045.
5) T. Nozoe, T. Mukai, M. Kunori, T. Muroi and K. Matsui, *Sci. Repts. Tohoku Univ., Ser.* **I**, 35, 242 (1951).
6) R. Fittig, W. Ahrens and L. Mattheides, *Ann.*, **147**, 36 (1868).
7) P. Akroyd, R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, **1951**, 3427.
8) T. Nozoe, T. Mukai and I. Murata, *Proc. Japan Acad.*, **28**, 142 (1952).
9) P. L. Pauson, *Chem. Revs.*, **55**, 9 (1955).
10) Y. Kitahara, *Sci. Repts, Tohoku Univ., Ser.* **I**, **39**, 250 (1956).

room temperature afforded yellow needles (XIa) which gave red coloration with ferric chloride. From its analytical value and the ultraviolet absorption spectrum (Fig. 2) it was assumed to be bis-(2-methyltropon-7-yl)-hydrazine (C) or its tautomer (C′) but no further study was made.

C C′

Similar treatment of IIb with hydrazine hydrate yielded colorless needles (XIIa) and yellow needles (XIb). The former was assumed to be 3-bromo-*o*-toluic acid hydrazide from its analytical value and its ultraviolet absorption spectrum (Fig. 2) and the latter to have the analogous structure to XIa. On the other hand, treatment of IIc with hydrazine hydrate gave 3,5-dibromo-*o*-toluic acid hydrazide (XIIb) and the compound corresponding to XIa and XIb was not obtained.

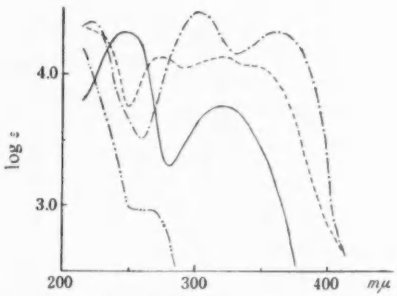


Fig. 2. Ultraviolet absorption spectra of VI (——), Xa (------), XIa (—·—·—) and XIIa (—··—··—) in methanol.

Several methods[11-15] have already been reported by which 2-halotropones could be converted to tropolones. Application of these methods to IIb and IIc gave no satisfactory results, but by heating of IIb and IIc each with sodium acetate in acetic acid[11] 4-bromo-3-methyltropolone (XIIIa) and 4, 6-dibromo-3-methyltropolone (XIIIb) were obtained respectively only with poor yields.

Experimental

Reaction of 3-Bromotropolone (Ia) and Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from 5.0 g. of methyl iodide, 0.84 g. of magnesium and 20 cc. of absolute ether, a solution of 2.0 g. of Ia dissolved in 20 cc. of dehydrated tetrahydrofuran was added in drops under stirring, while chilling with ice. The mixture was stirred for further five hours under ice-chilling, decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform solution was washed with dilute sodium hydroxide solution by which 320 mg. of Ia was recovered. The chloroform solution was then washed with water, dried and the solvent was removed to give 750 mg. of reddish brown oil. This oil was dissolved in benzene, passed through an alumina column, and 470 mg. of 7-bromo-2-methyltropone (IIa), m. p. 43~45°C, was obtained. Recrystallization from cyclohexane gave colorless plates, m. p. 46~47°C.

Found: C, 48.39; H, 3.90. Calcd. for C_8H_7OBr: C, 48.22; H, 3.54%.

Reaction of 7-Bromo-2-methyltropone (IIa) and Alkali.—A mixture of 50 mg. of IIa and 0.5 cc. of 1 N sodium hydroxide was heated on a water bath for one hour. After removal of the insoluble material, the aqueous layer was acidified with dilute hydrochloric acid and the crystals that separated out were recrystallized from dilute ethanol to give colorless crystals (IIIa), m.p. 99~101°C, undepressed at melting point on admixture with *o*-toluic acid.

Reaction of 3, 7-Dibromotropolone Methyl Ether (Ib) and Methylmagnesium Iodide.—To a solution of methylmagnesium iodide prepared from 3.0 g. of methyl iodide, 0.5 g. of magnesium and 30 cc. of absolute ether, a solution of 3.0 g. of Ib dissolved in 30 cc. of dehydrated benzene was added in drops and stirring was continued for further two and a half hours. The reaction mixture was poured into dilute sulfuric acid, and the yellow precipitates thereby obtained were filtered off. After washing the organic solvent layer with water, the solvent was removed to give 710 mg. of 3, 7-dibromo-2-methyltropone (IIb). By passing the oily portion through an alumina column 150 mg. of a second crop of IIb was obtained. Recrystallization from ethanol gave colorless needles, m. p. 121~122°C.

Found: C, 34.29; H, 2.29. Calcd. for $C_8H_6OBr_2$: C, 34.57; H, 2.18%.

Reaction of 3, 7-Dibromo-2-methyltropone (IIb) and Alkali.—Similar treatment of IIb with 1 N sodium hydroxide as in the case of IIa gave colorless plates (IIIb), m. p. 150°C. The reported melting point of 3-bromo-*o*-toluic acid is 153°C.

Found: C, 44.88; H, 3.45. Calcd. for $C_8H_7O_2Br$: C, 44.68; H, 3.28%.

IIIb was debrominated catalytically to *o*-toluic acid (IIIa), m. p. 100~102°C, and identified by a mixture melting point determination.

Reaction of 3, 5, 7-Tribromotropolone Methyl Ether (Ic) and Methylmagnesium Iodide.—a) To an ice-chilled solution of methylmagnesium iodide prepared from 1.52 g. of methyl iodide, 0.26 g. of magnesium and 15 cc. of absolute ether, 2.0 g. of Ic dissolved in 15 cc. of benzene was added under stirring. The mixture was stirred further for one

11) T. Nozoe, Y. Kitahara, T. Ando, S. Masamune and H. Abe, ibid., *Ser.* I, 36, 166 (1952).
12) W. E. Doering and J. R. Mayer, *J. Am. Chem. Soc.*, 75, 2387 (1953).
13) S. Seto, *Sci. Repts. Tohoku Univ., Ser.* I, 37, 275 (1953).
14) S. Seto, ibid., 37, 297 (1953).
15) W. E. Doering and C. F. Hiskey, *J. Am. Chem. Soc.*, 74, 5688 (1952).

hour and decomposed with dilute sulfuric acid. After washing the organic solvent layer successively with water, 5% sodium hydrogen carbonate solution and water, the solvent was removed and 2.1 g. of red oil was obtained. The oil was redissolved in a mixture of benzene and petroleum ether and passed through a silica column. Three kinds of crystals were thereby obtained; 670 mg. of 2-methyl-3, 5, 7-tribromotropone (IIc), m. p. 62~64°C; 80 mg. of 3, 5-dibromo-6-methyltropolone (IV), m. p. 148~150°C; 20 mg. of 3, 5-dibromo-2-methoxy-6-methyltropone (V), m. p. 147~149°C.

b) To a solution of methylmagnesium iodide prepared from 3.8 g. of methyl iodide, 4.0 g. of Ic dissolved in benzene was added. Treatment of the reaction mixture as in a) gave 920 mg. of IIc, 120 mg. of IV, 75 mg. of V and 20 mg. of dibromodimethyltropone (VI).

IIc was recrystallized from a mixture of benzene and petroleum ether to give colorless needles, m. p. 64~65°C.

Found: C, 27.26; H, 1.88. Calcd. for $C_8H_5OBr_3$: C, 26.92; H, 1.41%.

Pyridine solution of IIc gives a reddish purple coloration with dilute sodium hydroxide solution.

IV was recrystallized from a mixture of benzene and petroleum ether to give colorless needles, m. p. 151.5~153°C. Benzene solution of IV gives red coloration with ferric chloride.

Found: C, 32.95; H, 2.54. Calcd. for $C_8H_6O_2Br_2$: C, 32.68; H, 2.06%.

V was recrystallized from a mixture of benzene and petroleum ether to give colorless needles, m. p. 151~152°C. Pyridine solution of V colors reddish purple with dilute sodium hydroxide solution.

Found: C, 35.48; H, 3.00. Calcd. for $C_9H_8O_2Br_2$: C, 35.06; H, 2.60%.

VI was recrystallized from ethanol to yield colorless needles, m. p. 116~117°C. Pyridine solution gives deep reddish purple coloration with dilute sodium hydroxide solution.

Found: C, 36.96; H, 3.03. Calcd. for $C_9H_9OBr_2$: C, 36.98; H, 2.73%.

Reaction of 2-Methyl-3, 5, 7-tribromotropone (IIc) and Alkali.—Similar treatment of IIc with 2 N sodium hydroxide solution as in the case of IIa gave colorless crystals (IIIc), m. p. 195~197°C.

Found: C, 33.09; H, 2.36. Calcd. for $C_9H_6O_2Br_2$: C, 32.68; H, 2.06%.

IIIc was debrominated to *o*-toluic acid, m. p. 100~102°C.

Debromination of 3,5-Dibromo-6-methyltropolone (IV).—Catalytic reduction of 40 mg. of IV dissolved in 6 cc. of methanol, in the presence of 50 mg. of sodium acetate and 20 mg. of 5% palladium-charcoal resulted in absorption of 6 cc. of hydrogen. After removal of the catalyst by filtration, the solvent was removed and the crystalline residue was recrystallized from petroleum ether to give colorless crystals, m. p. 70~72°C. These crystals showed no depression at the melting point on admixture with 4-methyltropolone (VII).

Acid Hydrolysis of 3, 5-Dibromo-2-methoxy-6-methyltropone (V).—A suspension of 18 mg. of V in a mixture of 0.5 cc. of acetic acid and 0.1 cc. of hydrobromic acid (sp. g. = 1.48) was heated on a water bath for one hour. Addition of water separated 14 mg. of colorless crystals, m. p. 150~151°C. These crystals showed no depression at the melting point on admixture with 3, 5-dibromo-6-methyltropolone (IV).

Reaction of 3, 5-Dibromo-2-methoxy-6-methyltropone (V) and Alkali.—Similar treatment of V with dilute aqueous sodium hydroxide as in the case of IIa afforded colorless plates (VIII), m. p. 181~183°C, the melting point remaining unchanged on admixture of 4, 6-dibromo-*m*-toluic acid.

Reaction of Hydrazine and the Debromination Product of 3, 5-Dibromo-2-methoxy-6-methyltropone (V).—A solution of 60 mg. of V dissolved in 6 cc. of methanol was catalytically debrominated with the addition of 50 mg. of sodium acetate and 5% palladium-charcoal. After removal of the catalyst by filtration, the solution was diluted with water and extracted with benzene. The benzene layer was washed with water and the solvent was removed. The crystalline residue obtained was dissolved in 0.1 cc. of methanol and two drops of 80% hydrazine hydrate was added. The mixture was warmed on a water bath, cooled and the crystals thereby formed were recrystallized from benzene to give yellow needles, m. p. 121~123°C, which showed no depression at the melting point on admixture with 2-hydrazino-6-methyltropone (IX).

Reaction of 3, 5, 7-Tribromotropolone and Methylmagnesium Iodide.—To a solution of Grignard reagent prepared from 1.0 g. of methyl iodide, 0.72 g. of 3, 5, 7-tribromotropolone dissolved in dehydrated tetrahydrofuran was added under chilling with ice. After being stirred for five hours, the reaction mixture was decomposed with dilute sulfuric acid and extracted with chloroform. The chloroform extract was treated with dilute sodium carbonate solution by which 250 mg. of 3, 5, 7-tribromotropolone was recovered. The chloroform solution was further treated with dilute sodium hydroxide and the aqueous layer was acidified with dilute hydrochloric acid and extracted with benzene. Benzene extract afforded, after removal of the solvent, 130 mg. of dark red oil, chromatographic separation of which through an alumina column gave 40 mg. of crystals. Recrystallization from ethanol gave colorless plates, m. p. 133~134°C.

Found: C, 35.05; H, 3.25. Calcd. for $C_9H_{10}O_2Br_2$: C, 34.87; H, 3.25%.

These crystals showed no depression at the melting point on admixture of dimethyl 3, 5-dibromo-2-hydroxyphenyl carbinol prepared from the reaction of methyl 3, 5-dibromosalicylate and methylmagnesium iodide.

Reaction of 3, 7-Dibromotropolone Methyl Ether (Ib) and Ethylmagnesium Iodide.—To a solution of ethylmagnesium iodide, prepared from 3.2 g. of ethyl iodide, a solution of 3.0 g. of Ib in benzene was added with stirring at 0°C, and the reaction mixture was treated as in the reaction of Ib and methylmagnesium iodide. 3, 7-Dibromo-2-ethyltropone (IId) was obtained as colorless needles, m. p. 81~82°C. Yield, 730 mg.

Found: C, 37.28; H, 3.02. Calcd. for $C_9H_8OBr_2$: C, 36.98; H, 2.73%.

IId, when heated on a water bath for three hours,

with the addition of dilute aqueous solution of sodium hydroxide, was rearranged to give colorless plates (IIId), m. p. 100~101°C.

Found: C, 47.10; H, 4.00. Calcd. for $C_9H_9O_2Br$: C, 47.18; H, 3.96%.

IIId was catalytically debrominated to 2-ethylbenzoic acid (IIIe), m. p. 64~65°C.

Reaction of 3, 5, 7-Tribromotropolone Methyl Ether (Ic) and Ethylmagnesium Iodide.—To a solution of ethylmagnesium iodide, prepared from 1.68 g. of ethyl iodide, 2.0 g. of Ic in benzene was added. After being stirred for one hour under ice-chilling, the reaction mixture was treated as in the case of Ic and methylmagnesium iodide. With the recovery of 350 mg. of 3, 5, 7-tribromotropolone, 1.7 g. of dark red oil was obtained. This oil was dissolved in a mixture of benzene and petroleum ether and passed through a silica column, but none of each fraction of the eluents gave crystalline products.

The red oil (800 mg.), obtained from easily eluated fraction, was then warmed with a mixture of 1 cc. of ethanol and 1.5 cc. of 2 N sodium hydroxide for several minutes and chilled with ice. From the alkali-soluble part 220 mg. of dibromo-2-ethylbenzoic acid (IIIf) was obtained. Recrystallization from ethanol raised the melting point to 145~146°C.

Found: C, 35.01; H, 2.62. Calcd. for $C_9H_9O_2Br_2$: C, 35.10; H, 2.62%.

Alkali-insoluble part gave 300 mg. of ethyl dibromo-2-ethylbenzoate (IIIg). Recrystallization from ethanol raised the melting point to 45~46°C.

Found: C, 38.85; H, 3.57. Calcd. for $C_{11}H_{12}O_2Br_2$: C, 39.32; H, 3.60%.

IIIf was debrominated to 2-ethylbenzoic acid (IIIe), m. p. 63~64°C, and was esterified to IIIg with ethanol in the presence of concentrated sulfuric acid.

2-Methyl-7-(*p*-toluidino)-tropone (Xa).—A mixture of 50 mg. of 7-bromo-2-methyltropone (IIa) and 50 mg. of *p*-toluidine was heated at 120~130°C for ten minutes, diluted with benzene and the benzene solution was washed successively with dilute sulfuric acid and water. The crystalline residue, obtained upon removal of benzene, was recrystallized from ethanol to give yellow prisms, m. p. 75~76°C.

Found: N, 6.40. Calcd. for $C_{15}H_{13}ON$: N, 6.22%.

3-Bromo-2-methyl-7-(*p*-toluidino)-tropone (Xb).—Obtained from 3, 7-dibromo-2-methyltropone (IIb) and *p*-toluidine as in the case of Xa, and recrystallized from ethanol to give orange yellow prisms, m. p. 105~106°C.

Found: N, 4.89. Calcd. for $C_{15}H_{14}ONBr$: N, 4.59%.

7-Anilino-2-methyltropone (Xc).—Obtained from IIa and aniline as in the case of Xa as a red oil. Picrate of Xc was obtained by the usual method and recrystallized from methanol to give yellow microneedles, m. p. 159~160°C.

Found: N, 12.98. Calcd. for $C_{20}H_{16}O_8N_4$: N, 12.72%.

7-Anilino-3-bromo-2-methyltropone (Xd).—Obtained from IIb and aniline by the same method as above, and recrystallized from ethanol to give yellow crystals, m. p. 109~110°C.

Found: N, 4.95. Calcd. for $C_{14}H_{12}ONBr$: N, 4.83%.

Reaction of 7-Bromo-2-methyltropone (IIa) and Hydrazine.—To a solution of 50 mg. of IIa dissolved in 0.1 cc. of ethanol was added 50 mg. of 80% hydrazine hydrate. After being warmed slightly on a water bath, the reaction mixture was acidified with dilute sulfuric acid. Yellow crystals that separated were collected by filtration and recrystallized from ethanol and then from *n*-butanol to give yellow needles (XIa), m. p. 200~201°C. Ethanolic solution of XIa colors red with ferric chloride.

Found: C, 71.52; H, 5.91; N, 10.57. Calcd. for $C_{16}H_{16}O_2N_2$: C, 71.62; H, 6.01; N, 10.44%.

Reaction of 3, 7-Dibromo-2-methyltropone (IIb) and Hydrazine.—To a solution of 100 mg. of IIb dissolved in 0.6 cc. of benzene was added 100 mg. of 80% hydrazine hydrate and the whole was allowed to stand overnight. The crystals that separated out were recrystallized from ethanol to give colorless needles (XIIa), m. p. 157~158°C.

Found: N, 12.15. Calcd. for $C_8H_9ON_2Br$: N, 12.23%.

The filtrate was acidified with dilute sulfuric acid and the crystals that separated out were recrystallized from a mixture of dioxane and *n*-butanol to give yellow needles (XIb), m. p. 283~284°C.

Found: C, 45.10; H, 3.35. Calcd. for $C_{16}H_{14}O_2N_2Br_2$: C, 45.08; H, 3.31%.

Reaction of 2-Methyl-3, 5, 7-tribromotropone (IIc) and Hydrazine.—A solution of IIc in benzene was treated with hydrazine hydrate as in the case of IIb. The crystals obtained were recrystallized from ethanol to give colorless needles (XIIb), m. p. 175~176°C.

Found: N, 9.50. Calcd. for $C_8H_8ON_2Br_2$: N, 9.09%.

4-Bromo-3-methyltropolone (XIIIa).—A mixture of 100 mg. of IIb, 80 mg. of anhydrous sodium acetate and 1 cc. of glacial acetic acid was heated at 180~200°C for one hour. The solution was then diluted with water, warmed further for a half hour, extracted with benzene and the benzene solution was treated with dilute aqueous sodium hydroxide. Yellow sodium salt that separated out was collected by filtration and acidified with hydrochloric acid. XIIIa thereby liberated was recrystallized from ethanol to give pale brownish crystals, m. p. 100~102°C; yield was very poor (about 5 mg.). XIIIa gives red coloration with ferric chloride.

Found: C, 45.30; H, 3.27. Calcd. for $C_8H_7O_2Br$: C, 44.68; H, 3.28%.

4, 6-Dibromo-3-methyltropolone (XIIIb).—Obtained from 40 mg. of IIc as in the case of XIIIa and recrystallized from ethanol to give pale yellow needles, m. p. 121~123°C; yield was about 5 mg.

Found: C, 33.04; H, 2.59. Calcd. for $C_8H_6O_2Br_2$: C, 32.68; H, 2.06%.

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Syntheses and Reactions of 2-Bromomethyltropones

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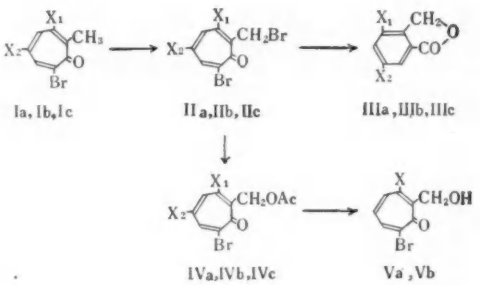
Recently it was reported that tropone, 2-phenyltropone and several kinds of their bromine substituted compounds were comparatively easily brominated on their tropone nucleus through addition of bromine to their double bonds and subsequent dehydrobromination (and debromination in some instances), showing the unsaturated properties of the tropone nucleus[1,2].

In the present paper the bromination of 7-bromo-2-methyltropone (Ia), 3, 7-dibromo-2-methyltropone (Ib) and 2-methyl-3, 5, 7-tribromotropone (Ic)[3] was undertaken. The aim of the experiment of this paper is twofold; (1) 2-methyltropone is considered to be a vinylog of methylketone and accordingly it would be important to examine whether bromination occurs on a tropone nucleus or on a methyl group; and (2) 2-bromomethyltropones, if they were obtained, would be easily converted to 2-hydroxymethyltropones, the key intermediates for the preparation of 2-formyltropones.

Application of one molecular equivalent of bromine or *N*-bromosuccinimide on Ia afforded pale yellow needles (IIa) in a good yield. Although attempted conversion of IIa to phthalide (IIIa) directly by treating with alkali failed, the structure of IIa was proved to be 7-bromo-2-bromomethyltropone as described later. Similarly, both Ib and Ic, when treated with bromine, afforded 2-bromomethyl-3, 7-dibromotropone (IIb) and 2-bromomethyl-3, 5, 7-tribromotropone (IIc), respectively. Treatment of IIb with dilute alkali gave 4-bromophthalide (IIIb)[4], which on reduction over palladium charcoal aforded IIIa. Similar treatment of IIc with alkali afforded 4, 6-dibromophthalide (IIIc), whose debromination gave IIIa.



Bromination of IIa gave pale yellow needles (IId), the structure of which is not clear yet. On the other hand, further bromination of IIb was found to be difficult even under prolonged heating on a water bath. This fact is rather interesting from the fact that 3, 7-dibromo-2-phenyltropone was easily brominated to give 2-phenyl-3, 5, 7-tribromotropone[1]. Ultraviolet absorption spectra of IIa, IIb and IIc were shown in Fig. 1.

Although the preparations and reactions of

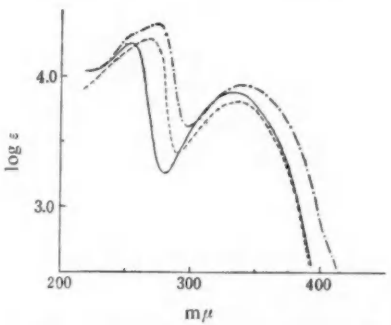


Fig. 1. Ultraviolet absorption spectra of IIa(——), IIb (----) and IIc(-·-·-) in methanol.

1) T. Mukai, *Sci. Repts. Tohoku Univ., Ser.* I, **38**, 280 (1954).
2) T. Nozoe, T. Mukai and K. Takase, ibid., **39**, 164 (1956).
3) K. Kikuchi, This Bulletin, **33**, 628 (1960).
4) J. Tirouflet, *Bull. soc. sci. Bretagne, Spec. No.*, **26**, 7 (1951); *Chem. Abstr.*, **47**, 8693 (1953).

hydroxymethyltropolone[5-7] and formyltropolone[7,8] derivatives have been examined in some detail, 2-hydroxymethyltropone and 2-formyltropone derivatives have remained unknown. Therefore, the synthesis of these materials were next attempted.

Application of silver acetate on IIa in acetic acid gave 2-acetoxymethyl-7-bromotropone (IVa) which, when heated with a mixture of dilute hydrochloric acid and ethanol, easily underwent hydrolysis to give 7-bromo-2-hydroxymethyltropone (Va). Va showed no coloration with ferric chloride characteristic of tropolone. The ultraviolet absorption spectrum of Va reveals that it retains tropone nucleus as shown in Fig. 2. Treatment of Va with dilute alkali gave IIIa though in a poor yield. These facts indicate that Va has the expected structure and that bromination of Ia has undoubtedly occurred on a side chain methyl group as described before.

Similar treatment of IIb with silver acetate or sodium acetate afforded 2-acetoxymthyl-3, 7-dibromotropone (IVb), which was hydrolyzed to 3, 7 - dibromo - 2 - hydroxymethyltropone (Vb). Similarly, treatment of IIc with silver acetate gave 2-acetoxymethyl-3, 5, 7-tribromotropone (IVc). Acid hydrolysis of IVc, however, resulted in the formation of IIIc. This result is curious compared with the fact that 2-halotropones usually do not rearrange to aromatic acids in acidic media.

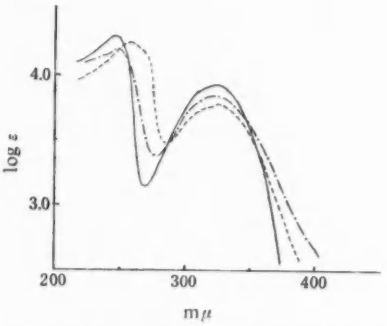
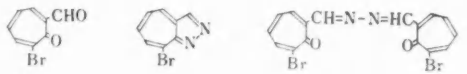


Fig. 2. Ultraviolet absorption spectra of Va(——), Vb(----) and VI(-·-·-) in methanol.

Mild oxidation of Va with activated manganese dioxide in benzene[8] or with chromium trioxide in a mixture of acetic acid and acetic anhydride afforded 7-bromo-2-formyltropone (VI). VI reduces ammoniacal silver nitrate solution and Fehling's solution and gives phenylhydrazone.

An attempted synthesis of 8-bromo-1, 2-diazaazulene (VII) by treating VI with hydrazine has not succeeded, and the only product was yellow crystals which was assumed to be symmetrical azine (VIII) of VI from its analytical value.



VI VII VIII

Experimental

7-Bromo-2-bromomethyltropone (IIa).—a) To a solution of 200 mg. of 7-bromo-2-methyltropone (Ia) in 1.5 cc. of acetic acid was added 170 mg. of bromine and the mixture was heated on a water bath for 30 min. and cooled. The crystals that separated were collected by filtration. Yield, 80 mg. Mother liquor was diluted with water, extracted with benzene and the benzene layer was washed successively with water, 2 N sodium carbonate and water. Removal of the solvent afforded second crop of 60 mg. of crystals. These crystals were combined and recrystallized from ethanol to give colorless needles (IIa), m. p. 103～104°C.

Found: C, 34.50; H, 2.07. Calcd. for $C_8H_6OBr_2$: C, 34.57; H, 2.18%.

b) A mixture of 520 mg. of Ia, 520 mg. of *N*-bromosuccinimide and 6 cc. of carbon tetrachloride was heated to reflux for four and one-half hours under irradiation. The crystals were filtered, washed well with benzene and the combined solution was washed with water. Removal of the solvent provided 500 mg. of crystals, m. p. 97～101°C. These crystals showed no depression of the melting point on admixture with IIa obtained by the method of a).

2-Bromomethyl-3, 7-dibromotropone (IIb).—A mixture of 100 mg. of 3, 7-dibromo-2-methyltropone (Ib), 0.8 cc. of acetic acid and 60 mg. of bromine was heated on a water bath for about 30 min. From the reaction mixture 110 mg. of IIb was obtained as pale yellow needles of m. p. 141～143°C. Recrystallization from ethanol raised the melting point to 142～143°C.

Found: C, 27.26; H, 1.88. Calcd. for $C_9H_5OBr_3$: C, 26.92; H, 1.41%.

2-Bromomethyl-3, 5, 7-tribromotropone (IIc).—To a solution of 200 mg. of 2-methyl-3, 5, 7-tribromotropone (Ic) dissolved in 1 cc. of acetic acid was added 100 mg. of bromine, and the mixture was heated on a water bath for about 30 min. On cooling, 220 mg. of IIc was obtained as pale yellow plates of m. p. 104～106°C. Recrystallization from ethanol raised the melting point to 107～108°C.

Found: C, 22.13; H, 1.14. Calcd. for $C_9H_4OBr_4$: C, 22.05; H, 0.93%.

Bromination of 7-Bromo-2-bromomethyltropone (IIa).—A mixture of 50 mg. of IIa and 35 mg. of bromine in 0.3 cc. of acetic acid was heated on a water bath for about 30 min. and cooled. The crystals that separated were collected by filtration and recrystallized from ethanol to give pale yellow needles

5) T. Nozoe, T. Mukai and K. Matsui, *Proc. Japan Acad.*, **27**, 561 (1951).
6) T. Nozoe, T. Mukai and K. Takase, *Sci. Repts. Tohoku Univ., Ser.* I, **36**, 40 (1952).
7) S. Seto and K. Ogura, This Bulletin, **32**, 493 (1959).
8) E. Sebe and S. Matsumoto, *Sci. Repts. Tohoku Univ., Ser.* I, **38**, 308 (1954).

(IId), m. p. 131～133°C. Yield, 45 mg. Further recrystallization from ethanol raised the melting point to 133～134°C.

Found: C, 27.56; H, 1.76. Calcd. for $C_9H_5OBr_3$: C, 26.92; H, 1.41%.

Action of dilute aqueous sodium hydroxide on IId gave only unidentified black resinous matter. Attempted debromination of side chain bromine with zinc and acetic acid also failed.

Attempted Bromination of 2-Bromomethyl-3, 7-dibromotropone (IIb).—A mixture of 50 mg. of IIb and 30 mg. of bromine in 0.4 cc. of acetic acid was heated for two hours on a water bath in a closed vessel. On cooling, 20 mg. of pale yellow crystals, m. p. 136～140°C was obtained and identified as starting material by the mixture melting point method. Mother liquor, on being diluted with water, gave pale yellow crystals of m. p. 113～125°C, purification of which was difficult.

Reaction of 2-Bromomethyl-3, 7-dibromotropone (IIb) and Alkali.—A mixture of 100 mg. of IIb and 1 cc. of 1 N sodium hydroxide solution was heated on a water bath for one hour, treated with active carbon and filtered. Acidification of the filtrate with dilute hydrochloric acid gave 35 mg. of 4-bromophthalide (IIIb) as colorless plates of m. p. 94～97°C. Recrystallization from cyclohexane raised the melting point to 98～99°C. Reported melting point of IIIb is 103～104°C.

Found: C, 45.39; H, 2.43. Calcd. for $C_8H_5O_2Br$: C, 45.10; H, 2.37%.

Catalytic debromination of IIIb afforded phthalide (IIIa), m. p. 70～71°C, undepressed of melting point on admixture with authentic sample.

Reaction of 2-Bromomethyl-3, 5, 7-tribromotropone (IIc) and Alkali.—A mixture of 100 mg. of IIc, 0.6 cc. of 1 N aqueous sodium hydroxide and 0.1 cc. of ethanol was treated as in the case of IIb, and 4, 6-dibromophthalide (IIIc) thereby obtained, was recrystallized from dilute ethanol to give colorless needles, m. p. 112～113°C.

Found: C, 33.15; H, 1.51. Calcd. for $C_8H_4O_2Br_2$: C, 32.91; H, 1.38%.

Debromination of IIIc afforded IIIa, m.p. 71～72°C.

2-Acetoxymethyl-7-bromotropone (IVa).—To a solution of 150 mg. of 7-bromo-2-bromomethyltropone (IIa) dissolved in 1.2 cc. of acetic acid 150 mg. of silver acetate was added, and the mixture was heated on a water bath for 15 min. with occasional stirring and filtered. Acetic acid was removed from the filtrate by evaporation, and the residue was extracted with benzene. The benzene solution was washed with water and the solvent evaporated. The crystals thereby obtained were recrystallized from a mixture of benzene and petroleum ether to give colorless needles (IVa), m. p. 108～110°C. Yield, 130 mg. Further recrystallization raised the melting point to 110～111°C.

Found: C, 46.30; H, 3.16. Calcd. for $C_{10}H_9O_3Br$: C, 46.72; H, 3.53%.

2-Acetoxymethyl-3,7-dibromotropone (IVb).—a) To a solution of 200 mg. of 2-bromomethyl-3, 7-dibromotropone (IIb) dissolved in 2 cc. of acetic acid was added 160 mg. of sodium acetate, the mixture was heated on a water bath for one and one-half hours and filtered. The filtrate was diluted with water, extracted with benzene, and the benzene extract was washed with water and concentrated. The crystals thereby obtained were recrystallized from ethanol to give colorless crystals (IVb), m. p. 84～87°C. Yield, 160 mg. Further recrystallization from ethanol raised the melting point to 88～89°C.

Found: C, 35.90; H, 2.30. Calcd. for $C_{10}H_8O_3Br_2$: C, 35.74; H, 2.40%.

b) Similar treatment of 200 mg. of IIb with 150 mg. of silver acetate as in the case of IIa afforded 150 mg. of colorless crystals of m. p. 85～88°C, undepressed of the melting point on admixture with IVb obtained in a).

2-Acetoxymethyl-3, 5, 7-tribromotropone (IVc).—Similar treatment of 300 mg. of 2-bromomethyl-3, 5, 7-tribromotropone (IIc) with 180 mg. of silver acetate as in the case of IIa afforded 240 mg. of IVc, m. p. 87～90°C. Recrystallization from ethanol gave colorless needles, m. p. 88～90°C.

Found: C, 28.59; H, 1.95 Calcd. for $C_{10}H_7O_3Br_3$; C, 28.95; H, 1.70%.

7-Bromo-2-hydroxymethyltropone (Va).—A solution of 330 mg. of 2-acetoxymethyl-7-bromotropone (IVa) dissolved in a mixture of 3 cc. of ethanol and 1.5 cc. of 2 N hydrochloric acid was heated to reflux for 50 min. Evaporation of most of ethanol afforded 260 mg. of pale brown crystals (Va), m. p. 116～118°C (decomp.). Recrystallization from dilute ethanol gave colorless needles, m. p. 120～121°C (decomp.).

Found: C, 44.92; H, 3.74. Calcd. for $C_8H_7O_2Br$: C, 44.68; H, 3.28%.

Reaction of 7-Bromo-2-hydroxymethyltropone (Va) and Alkali.—A mixture of 40 mg. of Va and 0.5 cc. of 1 N sodium hydroxide solution was heated on a water bath for 30 min. The resulting clear solution was acidified with hydrochloric acid, treated with charcoal, filtered while hot and cooled. Colorless plates, m. p. 69～71°C, thereby obtained, showed no depression of melting point on admixture with phthalide.

3, 7-Dibromo-2-hydroxymethyltropone (Vb).—A solution of 100 mg. of 2-acetoxymethyl-3, 7-dibromotropone (IVb) dissolved in a mixture of 1 cc. of ethanol and 0.5 cc. of 2 N hydrochloric acid was heated on a water bath for one hour. Similar treatment of the reaction mixture as in the case of Va afforded 70 mg. of Vb, m. p. 100～103°C (decomp.). Recrystallization from ethanol gave colorless crystals, m. p. 109～110°C (decomp.).

Found: C, 33.08; H, 2.20. Calcd. for $C_8H_6O_2Br_2$: C, 32.68; H, 2.06%.

Acid Hydrolysis of 2-Acetoxymethyl-3,5,7-tribromotropone (IVc).—A solution of 300 mg. of IVc dissolved in a mixture of 2 cc. of ethanol and 1 cc. of 2 N hydrochloric acid was heated on a water bath for two hours and cooled. The crystals thereby obtained were recrystallized from ethanol to give colorless needles, m. p. 112～113°C, which showed no depression of melting point on admixture with IIIc obtained by the action of alkali on IIc.

7-Bromo-2-formyltropone (VI).—a) To a solution of 200 mg. of 7-bromo-2-hydroxymethyltropone (Va) dissolved in 10 cc. of benzene was added 800 mg. of active manganese dioxide, and the mixture was stirred for two hours at room temperature and filtered.

Evaporation of the solvent afforded 100 mg. of VI, m. p. 147~149°C (decomp.). Recrystallization from ethanol gave yellow needles, m. p. 148~150°C (decomp.).

Found: C, 45.05; H, 2.74. Calcd. for $C_5H_3O_2Br$: C, 45.10; H, 2.37%.

b) To a suspension of 100 mg. of Va in a mixture of 0.3 cc. each of acetic acid and acetic anhydride was added 0.3 cc. of chromium trioxide solution (prepared by dissolving 1 g. chromium trioxide in a mixture of 5 cc. each of acetic acid and acetic anhydride) at room temperature. The solution was warmed at 35~45°C for 50 min., cooled and the crystals that separated out were collected by filtraton. Yield, 40 mg. Recrystallization from ethanol gave yellow needles, m. p. 146°C (decomp.).

Phenylhydrazone of 7-Bromo-2-formyltropone (VI).—To a solution of 50 mg. of VI dissolved in 2 cc. of ethanol was added a solution of 40 mg. of phenylhydrazine hydrochloride in 0.3 cc. of water at room temperature. Phenylhydrazone of VI was obtained as purple needles, m. p. 142°C (decomp.). It was difficult to recrystallize from usual organic solvents.

Found: C, 55.51; H, 3.53; N, 9.15. Calcd. for $C_{14}H_{11}ON_2Br$: C, 55.46; H, 3.66; N, 9.24%.

Azine (VIII) of 7-Bromo-2-formyltropone (VI).—To a solution of 50 mg. of VI dissolved in 2.5 cc. of ethanol was added a solution of 20 mg. of hydrazine hydrochloride in 0.3 cc. of water at room temperature. Azine (VIII) was obtained as yellow crystals, m. p. 147~148°C (decomp.), which were difficult to recrystallize from usual organic solvents.

Found: C, 45.72; H, 2.47; N, 6.49. Calcd. for $C_{16}H_{10}O_2N_2Br_2$: C, 45.55; H, 2.39; N, 6.64%.

The author wishes to express his sincere thanks to Professor T. Nozoe of Tohoku University for his guidance and encouragement throughout this work, as well as to Professor S. Seto, Assistant Professor Y. Kitahara and Assistant Professor T. Mukai of Tohoku University for their kind advice and suggestions. He is also grateful to Miss K. Kato for the measurements of ultraviolet absorption spectra and to Mr. S. Ohyama and Miss A. Iwanaga for the elemental analyses.

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Inorganic Extraction Studies on the System between Tri-n-butyl Phosphate and Hydrochloric Acid*

By Tomitaro ISHIMORI, Kenju WATANABE and Eiko NAKAMURA

(Received October 28, 1959)

During the course of the solvent extraction studies on fission products and actinide elements with TBP, it was felt that the behavior of other common elements ought to be clarified. In the present paper, is studied the behavior of about fifty chemical elements, ranging from sodium to curium, in the TBP-hydrochloric acid system.

Experimental

Sources of Materials.—Tributyl phosphate was purified in the usual way[1-3], and used without any dilution. Hydrochloric acid solutions were prepared by diluting commercial concentrated hydrochloric acid. The acidity was determined volumetrically if necessary.

Table I[4-8] shows the sources of radioactive tracers. Most of the imported tracers were used as received, whereas Y-90, Nb-95[7] and Ra-224 were prepared from imported Sr-90, Zr-95 and Th-228, respectively. Many other tracers were prepared by irradiating suitable targets in JRR-1. In order to avoid complication as far as possible, very pure materials were used as the targets. The subsequent chemical treatments were carried out if necessary; however, in many cases targets were simply dissolved in acids and converted into chloride solutions.

The radiochemical purities were checked by γ-ray spectrometry, tracing the decay and/or β absorption. Nickel and cadmium tracers contained some radiochemical impurities. Accordingly these tracers were measured at photopeaks using a γ-spectrometer.

* TBP

1) K. Alcock, S. S. Grimley, T. V. Healy, J. Kennedy and H. A. C. McKay, *Trans. Faraday Soc.*, **52**, 39 (1956).
2) D. F. Peppard, G. W. Mason and J. L. Maier, *J. Inorg. & Nuclear Chem.*, **3**, 215 (1956).
3) D. F. Peppard, W. J. Driscoll, R. J. Sironen and S. McCarty, ibid., **4**, 326 (1957).
4) T. Ishimori, K. Yoshihara and H. Nakamura, 3rd Japan Conference on Radioisotope, S-17 (1959).
5) T. Ishimori, H. Nakamura, and E. Nakamura, ibid., S-16 (1959).
6) N. Shibata and K. Yoshihara, This Bulletin, **32**, 422 (1959).
7) S. Yajima, ibid., **31**, 699 (1958).
8) H. Ebihara and K. Yoshihara, ibid., **33**, 116 (1960).

Fig. 1. HCl—100% TBP acid dependence.

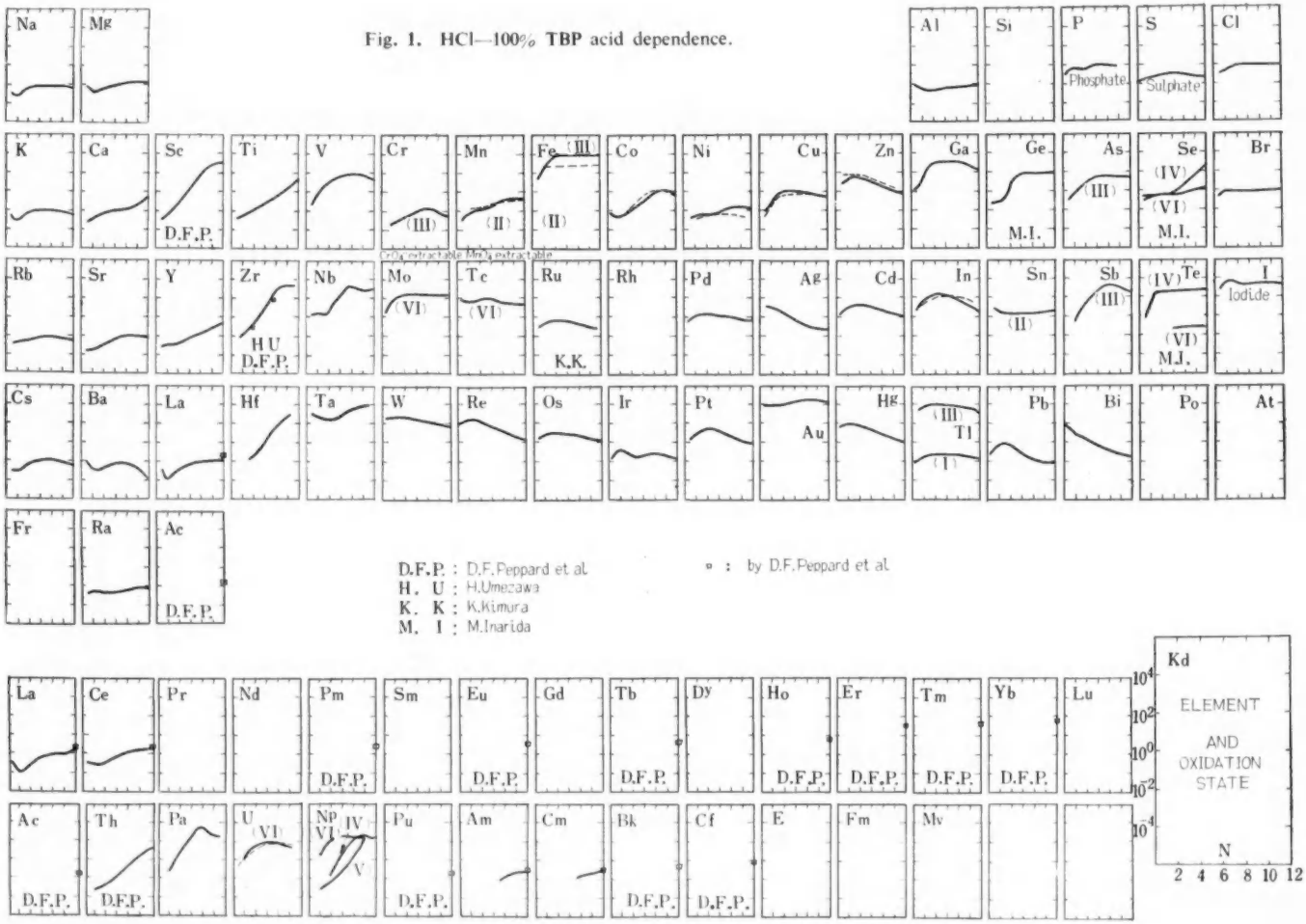
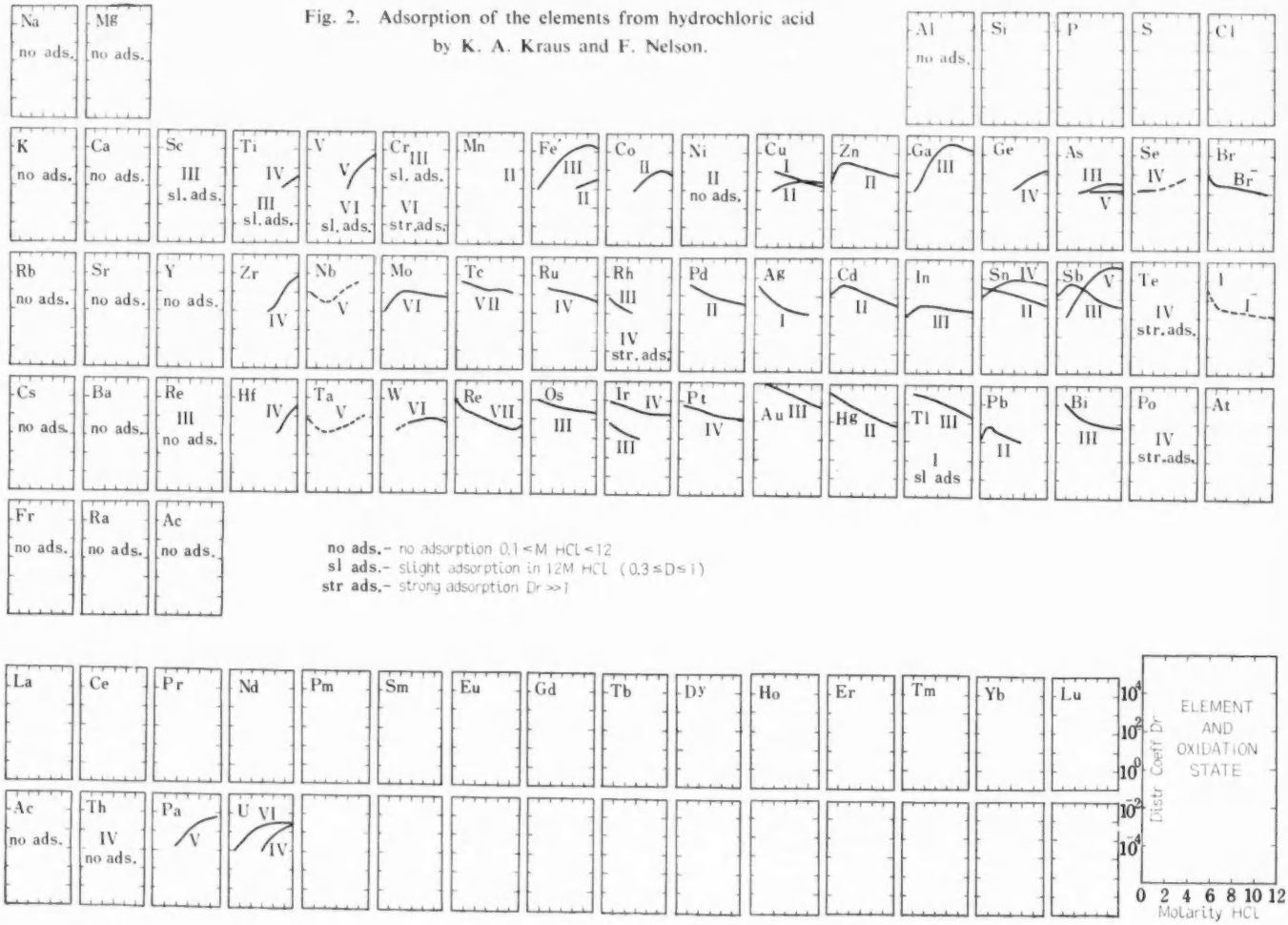


Fig. 2. Adsorption of the elements from hydrochloric acid
by K. A. Kraus and F. Nelson.



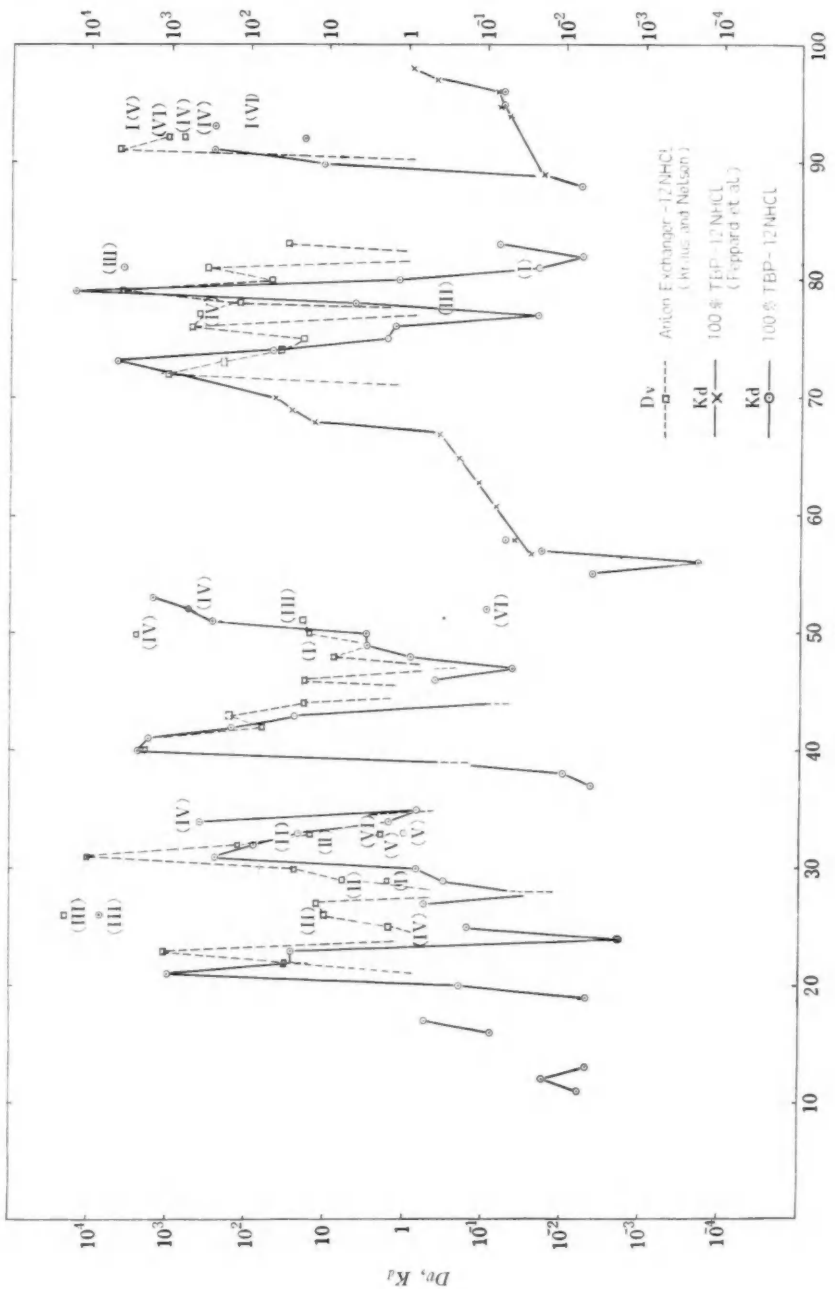


Fig. 3. Solvent extraction and anion exchange at 12 N HCl.

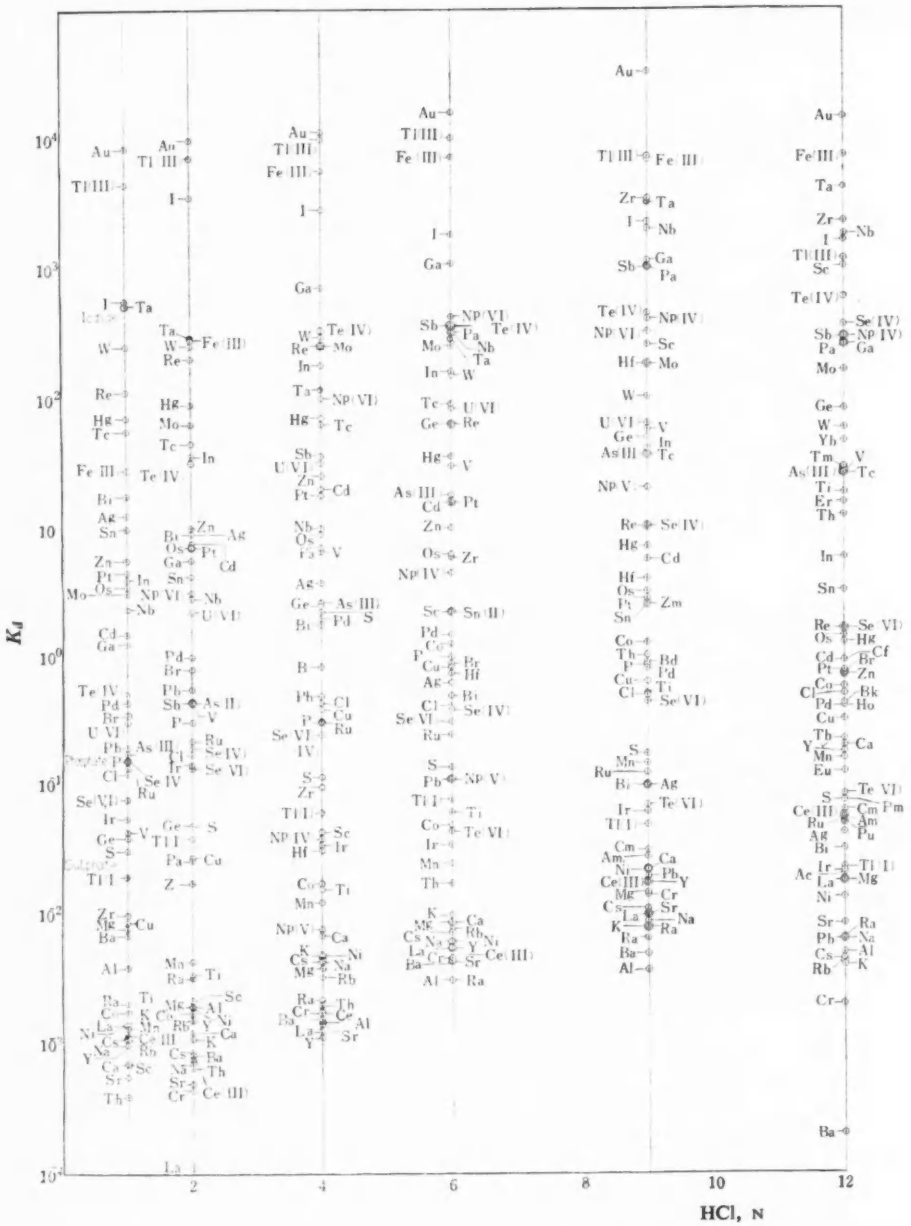


Fig. 4. K_d values in 100% TBP- 1~12 N HCl.

TABLE I. SOURCES OF RADIOACTIVE TRACERS USED

Element	Tracer	Target	Radiochemical purity was checked by	Remarks
Na	Na-24	Na_2CO_3	γ-spectrum, β-decay	
Mg	Mg-27	Mg metal	γ-decay	
Al	Al-28	Al metal	γ-decay, γ-spectrum	
P	P-32	S	β-decay, absorption	Processed, used as PO_4[4]
S	S-35	BHC	β-decay, absorption	Processed, used as SO_4[5]
Cl	Cl-38	NH_4Cl	γ-decay	
K	K-42	K_2CO_3	γ-spectrum, β-decay	Prepared by Isotope Production Group, JAERI
Ca	Ca-45			Imported
Ti	Ti-51	$Ti(OH)_4$	γ-decay	
V	V-52	NH_4VO_3	γ-decay	
Cr	Cr-51			Prepared by Yoshihara[6], Isotope Production Group, JAERI
Mn	Mn-56	MnO_2	γ-decay	
Fe	Fe-59			Imported
Co	Co-60			Imported
Ni	Ni-65	$Ni(NO_3)_2$		Counted at 1.49 MeV.
Cu	Cu-64	Cu metal	γ-decay, γ-spectrum	
Zn	Zn-65			Imported
Ga	Ga-72	Ga_2O_3	β-decay, γ-spectrum	
As	As-76	As_2O_3	β-decay, γ-spectrum	
Br	Br-80 m, 82	NH_4Br	γ-decay	
Rb	Rb-86, 88	RbCl	γ-decay	Cl-38 was removed by ion exchange
Sr	Sr-90			Imported
Y	Y-90		β-decay, absorption	Milked from imported Sr-90*
Nb	Nb-95		β-decay, absorption	Milked from imported Zr-95[7]
Mo	Mo-99	$(NH_4)_2MoO_4$	β-decay	
Tc	Tc-99			Imported
Pd	Pd-109	Pd metal	γ-decay	Ag-111 was removed by pptn. of AgCl after addition of Ag carrier
Ag	Ag-108	$AgNO_3$	γ-decay	
Cd	Cd-115	Cd metal	γ-spectum	Counted at 0.5~0.525 MeV.
In	In-116 m	In metal	γ-spectrum, β-decay	Prepared by Yoshihara, Isotope Production Group, JAERI
Sn	Sn-121	Sn metal		
Sb	Sb-122	Sb metal	γ-decay	
I	I-131			Imported
Cs	Cs-137			Imported
Ba	Ba-139	$BaCO_3$	γ-decay	
La	La-140	La_2O_3	γ-decay	
Ce	Ce-144			Imported
Hf	Hf-181			Imported
Ta	Ta-182			Imported
W	W-187, 185	W-oxinate	β, γ-decay	Prepared by Ebihara[8], Isotope Production Group, JAERI, hotchemically
Re	Re-186, 188	Re metal	γ-decay	
Os	Os-191, 193	Os metal	γ-decay	
Ir	Ir-192, 194	Ir metal	β, γ-decay	Fused with Na_2O_2
Pt	Pt-193, 197	Pt metal	β, γ-decay	Au-199 was removed*
Au	Au-198	Au metal	γ-spectrum, β-decay	Prepared by Yoshihara, Isotope Production Group, JAERI
Hg	Hg-203			Imported
Tl	Tl-204			Imported
Ra	Ra-224		α-decay	Milked from Th-228*

* Procedures are given in the present paper.

Inorganic extraction,
in 100% TBP—HCl system
TBP extraction of,
Na, Mg, Al, PO_4, SO_4, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce and other rare earth elements, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Ra, Th, Pb, Bi, Ra, Th, Pa, U, Np, Am and Cm

The specific activity of these radiochemical tracers were higher than 10^4 cpm/100 microgram. Although in some cases the oxidation states and the chemical forms of the tracer could not be clearly defined, for the most part familiar chemical forms were chosen as far as possible.

Distribution ratios were determined radiometrically in the ordinary way[2,3,9].

Results and Discussion

The results obtained are summarized in Fig. 1 as a series of graphs of $\log K_d$ vs. N HCl, where K_d is the distribution ratio and N the molarity. Fig. 1 was compiled from some published and unpublished results. Curves for scandium[2], zirconium[2], some of the rare earth elements[10,11], thorium[2] and some other actinide elements[10,11] are taken from the work of Peppard and his coworkers. Data for zirconium[12], ruthenium[13], germanium[14], selenium[14] and tellurium[14] are taken from the observations of Umezawa et al., Kimura and Inarida. The curves for lead, bismuth, uranium, americium and curium were obtained by one of the present authors (T. Ishimori) during his stay in the Argonne National Laboratory, Lemont, Ill. U.S.A. Finally the three curves for neptunium (IV), (V) and (VI) are quoted from the previous paper[9]. The curves for iron, cobalt, nickel, copper, zinc, indium and uranyl obtained by Irving et al.[15] are added to Fig. 1 with broken lines. Morris and Bell[16] gave the acid dependence curve for cobalt which coincides with that of the present authors. It is likely that permanganate and chromate have fairly high K_d values. However, their values were not plotted because of the rapid reduction of these ions in the system.

As Fig. 1 shows, the four alkali metal elements behave in a similar way, showing always very low K_d values. Halogen elements keep their K_d values practically constant in the higher acidity range over 4 N. There are some similarities in the shapes of the acid dependence curves for zinc, cadmium and bivalent mercury; ruthenium, palladium, osmium and platinum; and tervalent arsenic and antimony, respectively.

The K_d values of scandium, yttrium and lanthanum increase with their decreasing atomic number, Z, at higher acidity range. A similar relationship is seen more clearly among quadrivalent zirconium, hafnium and thorium. In these cases, the element of smaller Z has higher K_d value. On the other hand, the extractability of alkali metal elements or the group of zinc, cadmium and bivalent mercury, does not depend on the value of Z. Further, K_d values of chloride, bromide and iodide increase with their increasing atomic number.

Fig. 2 gives the adsorption behavior of the elements on an anion exchange resin from hydrochloric acid solutions. The curves in Fig. 2 are rewritten in a similar scale with that of Fig. 1 based on the original figure proposed by Kraus and Nelson[17]. As they did not give distribution coefficients, D_v, less than 1, the curves below $D_v=1$ are not drawn in Fig. 2.

The shapes of the acid dependence curve given in Figs. 1 and 2 are very similar for most elements. The high K_d value of scandium is a rare exception. It is not understandable that the solvent-extraction behavior of tervalent antimony resembles the ion exchange behavior of quinquevalent antimony.

It is likely that the resemblance discussed above shows similar mechanisms of distribution between the anion exchange and the extraction with TBP.

The K_d values at 12 N hydrochloric acid were plotted against the atomic number, Z, in Fig. 3. The figure shows that the K_d values vary regularly to some extent, giving two peaks for one long period of the periodic table. The values for lanthanide and tervalent actinide elements are quoted from the work of Peppard et al.[2,10,11] who found the effect of the half-filled shell in the relationship between K_d and Z.

The broken lines in Fig. 3 show the relationship between D_v values of anion exchange and Z. A close similarity is seen here again between the behaviors of the solvent extraction and the ion exchange.

Fig. 4 gives K_d values in the 100% TBP-hydrochloric acid system. This will be convenient for checking the possibility and efficiency

9) T. Ishimori and E. Nakamura, ibid., 32, 713 (1959).
10) D. F. Peppard, P. R. Gray and M. M. Markus, *J. Am. Chem. Soc.*, 75, 6063 (1953).
11) P. R. Gray, unpublished results quoted in E. K. Hyde, "Proceedings International Conference on Peaceful Uses of Atomic Energy, Geneva", Vol. VII, P/728, United Nations Publication, New York (1956).
12) T. Ishimori, H. Umezawa and K. Watanabe, *J. Atomic Energy Soc. Japan*, 1, 299 (1959).
13) K. Kimura, unpublished.
14) M. Inarida, unpublished.
15) H. Irving and D. N. Edgington, *J. Inorg. & Nuclear Chem.*, 10, 306 (1959).
16) D. F. C. Morris and C. F. Bell, ibid., 10, 337 (1959).
17) K. A. Kraus and F. Nelson, "Proceedings International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955", Vol. VII, P/837, United Nations Publication, New York (1956).

of a mutual separation of a couple of elements chosen arbitrarily. These K_d values are found with tracers of fairly high specific activities. Therefore, optimum conditions of a separation found in Fig. 4 will fit farily well in a tracer scale chemical separation; however, some caution must be exercised in macro-scale separations. For example, K_d for silver of more than 10 at 1 N acidity, is not applicable in a macro-scale separation because of the formation of insoluble silver chloride. Some examples are given in the following, showing how to utilize the K_d values obtained.

Applications

a) Preparation of Y-90 (or La-140).—The solvent extraction behavior of strontium, yttrium, barium, lanthanum and iron in the 100% TBP-hydrochloric acid system are given in Fig. 5. The curves of Fig. 5. show that the direct separation of Y-90 (or La-140) from Sr-90 (or Ba-140) is not easy. However, the difference between K_d values for iron and yttrium (or lanthanum) is so great that yttrium (or lanthanum) is separated from iron very easily. Yttrium-90 (or La-140) is separated from Sr-90 (or Ba-140) by the carrying down with ferric hydroxide. The precipitate is dissolved in 3 N hydrochloric acid. The TBP extraction

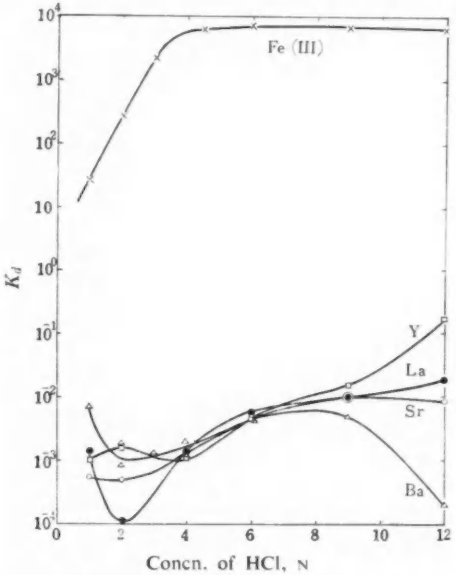


Fig. 5. The K_d valuer of iron, strontium, yttrium, barium and lanthanum.
—×— Fe, —○— Sr, —□— Y,
—△— Ba, —●— La

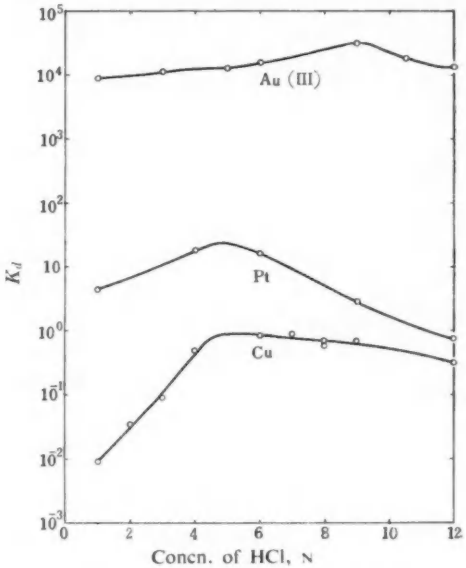


Fig. 6. The K_d values of gold, plutinum and copper.

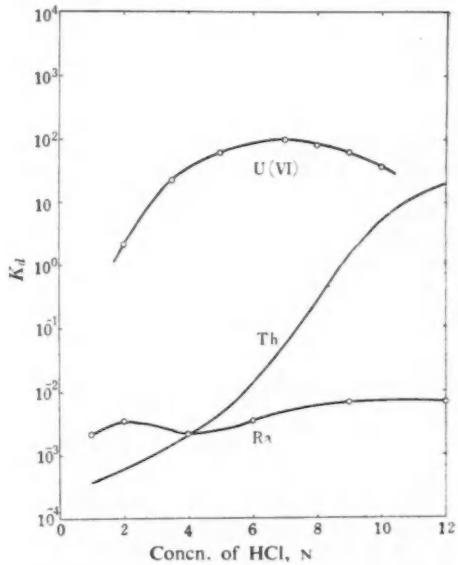


Fig. 7. The K_d values of uranium, thorium and radium in HCl-100% TBP.
The data for thorium was taken from the work of Peppard et al.

removes iron, leaving Y-90 (or La-140) carrier free in the acid solution.

b) Radiochemical Purification of Pt-197.— The difference of K_d values between gold and platinum is shown in Fig. 6. As is seen in the figure, K_d values of platinum are too high to keep platinum in the acid quantitatively. Therefore, TBP is diluted with toluene in order to make K_d values for both elements lower. The TBP (1 : 2) works well for the separation of gold from platinum at 1 or 12 N hydrochloric acid.

Irradiated platinum containing Pt-197 and Au-199 is dissolved in aqua regia, and converted into 1 or 12 N hydrochloric acid solution. Extraction of Au-199 with TBP (1 : 2) brings about an aqueous solution of purified Pt-197 tracer. Gold in copper is removed similarly with diluted TBP from 1 N hydrochloric acid solution. (Fig. 6).

c) Milking of Th-234 from U-238. — The difference between K_d values for thorium and uranyl ion is shown in Fig. 7.

In the 6 N hydrochloric acid—TBP system uranyl ion is extracted into TBP, whereas thorium remains in the aqueous solution. The TBP solution of uranyl chloride is used conveniently as a cow. In this case the addition of a small amount of bromine prevents the photoreduction of uranyl ion.

d) Milking of Ra-244 from Th-228.—As is shown in Fig. 7, radium is not extracted from 12 N hydrochloric acid, while thorium is extractable with a K_d of about 10. Accordingly radium is left in the acid solution after several extractions of thorium with TBP. Both Pb-212 and Bi-212 remain in the acid solution with Ra-224.

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The Aconite Alkaloids. XXXIII. On Lucidusculine. III***

By Takashi AMIYA

(Received October 27, 1959)

In the previous reports some derivatives of lucidusculine (I), $C_{24}H_{35}O_4N$, have been reported and the extended formula of compound I has been proposed[2,3].

Lately the author has investigated the behavior of compound I toward various oxidizing agents, and the previously proposed partial formula[2] is further extended.

Oxidation of compound I with 3% hydrogen peroxide gave lucidusculine *N*-oxide-a (II), $C_{24}H_{35}O_5N \cdot H_2O$, m. p. 191°C (decomp.) in a poor yield. From the procedure for its preparation, compound II seems to contain water of crystallization[4-7].

Further, in order to obtain an epoxide derivative of compound I, perbenzoic acid oxidation has been performed. This oxidation has not given the results expected in the cases of Senecio alkaloids[8] and atisine derivatives[9]. Compound I reacted with only one mole of perbenzoic acid under different conditions and an *N*-oxide, lucidusculine *N*-oxide-b (III), $C_{24}H_{35}O_5N \cdot 1/2H_2O_2$***, m. p. 200°C (decomp.), was yielded. This reaction proceeds similar to that of strychnine[10]. Compound III lost hydrogen peroxide of crystallization on standing for several months, being converted into lucidusculine *N*-oxide-c (IV), $C_{24}H_{35}O_5N$, m. p. 209°C**** (decomp.)[5]. Infrared spectrum of compound

* This paper constitutes a part of a series entitled "The Aconite Alkaloids" by H. Suginome. Part XXX, cf. Foot Note 2). Part XXXII, cf. Foot Note 3).

** Part XXXII corresponds to part II of "On Lucidusculine". A preliminary note on part of the matter of this paper appeared in this Bulletin[1].

1) T. Amiya, This Bulletin, **30**, 677 (1957).
2) H. Suginome, T. Amiya and T. Shima, ibid., **32**, 824 (1959).
3) T. Amiya, ibid., **32**, 1133 (1959).
4) K. Bodendorf and B. Binder, *Arch. Pharm.*, **287**, 326 (1954).
5) D. W. Henry and E. Leete, *J. Am. Chem. Soc.*, **79**, 5254 (1957).
6) A. S. Bailey and R. Robinson, *J. Chem. Soc.*, **1948**, 703; R. H. F. Manske and H. L. Holmes, "The Alkaloids", Vol. II, Academic Press, Inc., Publishers, New York (1952), p. 522.
7) M. Oesterlin, *Ber.*, **76**, 224 (1943).
8) L. J. Dry, M. J. Koekemoer and F. L. Warren, *J. Chem. Soc.*, **1955**, 59.
9) C. F. Huebner and W. A. Jacobs, *J. Biol. Chem.*, **170**, 515 (1947).

*** Compound III does not contain water of crystallization[1] but does contain hydrogen peroxide.

10) M. Kotake and T. Mitsuwa, *J. Chem. Soc. Japan*, **57**, 236 (1936); R. N. Chakravarti and R. Robinson, *J. Chem. Soc.*, **1947**, 78.

**** The previously reported d. p. is revised to this.

IV showed a band at 10.47μ characteristic of an *N*-oxide group[11,12]. Its ultraviolet absorption spectrum showed only end absorption.

Compound III was readily reduced with zinc dust and dilute sulfuric acid to compound I normally.

Oxidation of compound I with *N*-bromosuccinimide afforded dehydrolucidusculine (V), $C_{24}H_{33}O_4N$, m. p. 175~180°C, with loss of two hydrogens. Its infrared spectrum showed sharp bands at 10.15 and 11.34μ which were probably indicative of a cyclic ether[13,14]. Compound I lacks the bands corresponding to these (10.15 and 11.34μ) of compound V. It is, therefore, probable that the reaction proceeds as in the case of each delcosine[13] and delsoline[14] with formation of a cyclic carbinolamine internal ether between carbinolamine hydroxyl and one of the hydroxyls in compound I. This may be supported by the fact mentioned below that lucidusculine *N*-oxide was found to change to compound V. Its ultraviolet absorptions spectrum showed end absorption.

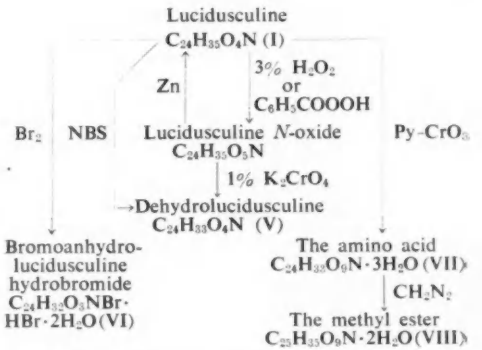
Strychnine *N*-oxide has been rearranged to a carbinolamine, pseudostrychnine[6]. Crow[15] mentioned the transformation of sparteine *N*-oxide to three possible carbinolamines. Therefore compound III was treated under the same conditions as in the case of the isomerization of strychnine *N*-oxide. Although an expected carbinolamine was not obtained, compound V was yielded. From these facts, it is supposed that an initially formed carbinolamine is changed to compound V with loss of one mole of water and with simultaneous formation of a carbinolamine internal ether.

In contrast to isoatisine[9], on bromination of compoud I no expected dibromo derivative was obtained. In this case a hydrobromide of a monobromo derivative, bromoanhydrolucidusculine hydrobromide (VI), $C_{24}H_{32}O_3NBr \cdot HBr \cdot 2H_2O$, m. p. 210°C (decomp.) was produced. Thus, the behavior of compound I on bromination is noted. Its infrared absorption spectrum showed the disappearance of a band which was characteristic of a terminal methylene group and corresponded to that (11.07μ)[16] of compound I[3]. From the observation of the molecular formula and its infrared spectrum, compound VI is perhaps yielded from an intermediate dibromo derivative, which is produced from compound I by the normal addition of one mole of bromine to a terminal methylene group, with simultaneous elimination of one mole each of water and hydrogen bromide. The ultraviolet absorption spectrum of compound VI does not correspond to that of a conjugated diene (Fig. 1). Although some interpretation of this observation might be presented, it will be left to a later occasion.

The oxidation of some of the aconite alkaloids, viz., atisine, isoatisine, kobusine and hypognavine with chromium trioxide-pyridine complex has been reported to give α, β-unsaturated ketone bases[19-21]. Furthermore, delpheline and lucaconine have been shown to be oxidized to lactams[22,23] by the same reagent.

On the other hand, the action of chromium trioxide-pyridine complex on compound I yielded an amino acid, $C_{24}H_{33}O_9N \cdot 3H_2O$, (VII), which showed no definite m. p. nor d. p., and gradually

TABLE I



11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd. Ed., Methuen & Co., Ltd., London (1958), p. 308.
12) R. H. Wiley and S. C. Slaymaker, *J. Am. Chem. Soc.*, **79**, 2233 (1957).
13) R. Anet, D. W. Clayton and Léo Marion, *Can. J. Chem.*, **35**, 397 (1957).
14) F. Sparatore, R. Greenhalgh and Léo Marion, *Tetrahedron*, **4**, 157 (1958).
15) See A. Albert, G. M. Badger and C. W. Shoppee, "Current Trends in Heterocyclic Chemistry", Butterworths Scientific Publications, London (1958), p. 116.
16) From the observation of infrared spectra of luciculine[2,8] and isoluciculine[17], of two bands near wavelength 11μ the one at 11.02μ corresponds to that of the terminal methylene group of luciculine, whilst the other at 11.27 μ[2,3] does not correspond. Normally, each of the compounds of the type $R_1R_2C=CH_2$[18] shows a band due to a terminal methylene group near this wavelength (11.27 μ). This shift from the normal wavelength is explicable by the fact that luciculine includes an allyl alcohol moiety, HO—C(H)—C=CH_2[17] which contains a polar group in the α-carbon atom to the double bond[18]. Similarly, a band characteristic of a terminal methylene group of compound I is not that at 11.26 μ[3] but that at 11.07 μ. Furthermore, lucidusculine diacetate, luciculine methiodide, isomesoluciculine and bromolucidusculine cyanamide[3] show the bands attributable to the terminal methylene groups at 11.07, 10.98, 11.03 and 10.95 μ in the infrared spectra, respectively.
17) T. Amiya, This Bulletin, **32**, 421 (1959).
18) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd. Ed., Methuen & Co., Ltd., London (1958), p. 51.
19) W. A. Jacobs and S. W. Pelletier, *J. Am. Chem. Soc.*, **76**, 4496 (1954).
20) T. Okamoto, *Chem. Pharm. Bull.*, **7**, 44 (1959).
21) S. Sakai, ibid., **7**, 51 (1959).
22) R. C. Cookson and M. E. Trevett, *Chem. & Ind.*, 1954 1324 ; *J. Chem. Soc.*, **1956**, 2689.
23) T. Amiya and T. Shima, This Bulletin, **31**, 1083 (1958).

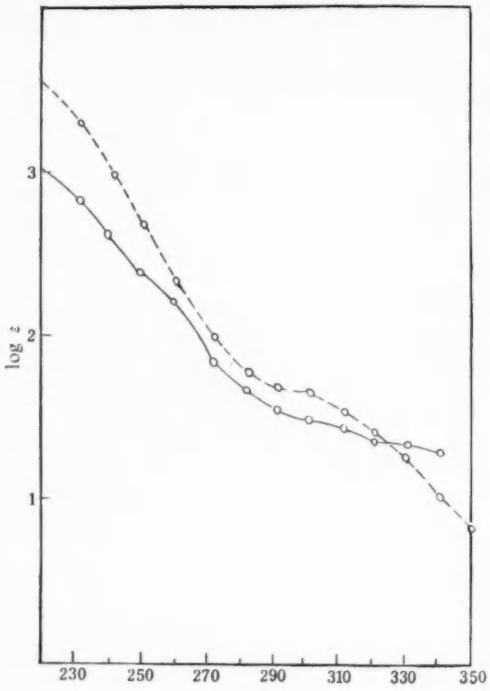


Fig. 1.

The amino acid (VII) --○--○--
Bromoanhydroluciduscuiline hydrobromide (VI) —○—○—

became black above 350°C. It is soluble in methanol and water but insoluble in ethanol and almost all other organic solvents. Although it showed no characteristic absorption maximum of a ketone carbonyl group in the ultraviolet spectrum (Fig. 1), its infrared spectrum showed a strong absorption near 5.85μ, indicating the presence of a ketone carbonyl group in a six-membered ring.

Methylation of compound VII with diazomethane gave a methyl ester (VIII), $C_{25}H_{35}O_9N \cdot 2H_2O$, which gradually swelled with decomposition near 288°C. The ultraviolet spectrum of compound VIII is similar to that of compound VII.

The oxidation of compound I with this milder reagent appears to convert the primary hydroxyl group to a carboxyl group as in the case of oxidation of a dodecahydrophenanthrene derivative[24], and probably the secondary one to the above mentioned ketone carbonyl group. Furthermore, the examination of the molecular formula, $C_{24}H_{33}O_9N \cdot 3H_2O$, and the infrared absorption spectrum of compound VII suggest that this oxidation reaction may cause formation of four new hydroxyl groups. Two of them seem to be introduced into the terminal methylene group as a vicinal glycol system. This is supported by the infrared absorption specteum of compound VII. The spectrum does not indicate a band due to a terminal methylene group near 11μ.

These results indicate that, of two hydroxyl groups in compound I, one is primary, and the other is secondary and is attached to a carbon atom in a six-membered ring.

Subsequently, the previously proposed partial formula[2] of I may be further summarized as[25],

$$C_{16}H_{20}\begin{cases} CH_2OH \\ OCOCH_3 \\ CH(OH) \\ N\text{-}C_2H_5 \\ C\text{=}CH_2 \end{cases}$$

Lucidusculine (I)

Experimental

Lucidusculine *N*-Oxide-a (II).—Powdered lucidusculine (0.5 g.) was suspended in 50 cc. of about 3% hydrogen peroxide and stirred under warming. After one hour the base was dissolved, and the resulting solution was further stirred for 1.5 hr. without warming. The excessive hydrogen peroxide was then decomposed in contact with a small quantity of freshly prepared manganese dioxide. After removal of the manganese dioxide, the solution was further decolorized with active carbon. After removal of the active carbon by filtration, the solution was evaporated to dryness in vacuo, and the residue was crystallized from aqueous methanol. It was recrystallized from methanol. It showed m. p. 191°C (decomp.).

Found: C, 65.94; H, 8.37; H_2O, 3.31. Calcd. for $C_{24}H_{33}O_9N \cdot H_2O$: C, 66.18; H, 8.56; H_2O, 4.13%.

From the above described procedure, it is probable that the substance does not contain hydrogen peroxide but water of crystallization as strychnine *N*-oxide does[6,7].

Lucidusculine *N*-Oxide-b (III).—Lucidusculine (0.5 g.) dissolved in chloroform (10 cc.) was added to 12 cc. of chloroform solution of perbenzoic acid (about 4 mol. equiv.). The reaction mixture was allowed to stand in a refrigerator for 6 days, and then was evaporated to dryness. To the residue, ether, about 1 cc. of 2 N hydrochloric acid and a small quantity of water were simultaneously added and the mixture was shaken. The aqueous layer separated from ether layer was passed through a column 17 cm. by 2 sq. cm. of anion-exchange resin (Amberite IRA-400) and then the column was eluted with 100, 50 and 25 cc. of water one after the other. From the first fraction (100 cc.) of elute, the residue was obtained, which gave crystals, m. p. 193°C

24) G. I. Poos, W. F. Johns and L. H. Sarett, *J. Am. Chem. Soc.*, 77, 1026 (1955).

25) The partial formula of I in a previous report[1] is revised to this.

(decomp.), on treatment with methanol. On recrystallization from methanol a material, m. p. 200°C (decomp.), $[\alpha]_D^{15}$ −101°, was obtained.

Found: C, 65.30, 65.52; H, 8.53, 8.68. Calcd. for $C_{24}H_{35}O_5N.{}^1/_2H_2O_2$: C, 66.32; H, 8.34%.

From the results described below it seems to contain hydrogen peroxide of crystallization. However, this material should be re-examined more precisely by iodometric titration.

Lucidusculine *N*-Oxide-c (IV).—To lucidusculine (1 g.) dissolved in 10 cc. of chloroform, were added 12 cc. of chloroform solution, containing excessive perbenzoic acid, and a few drops of water. After standing overnight, the chloroform was removed. The residue was digested with ether. To the ether-insoluble portion, 2 cc. of 2 N hydrochloric acid, water and chloroform were simultaneously added, and the mixture was shaken. The aqueous layer separated from chloroform layer was passed through the above mentioned column of anion-exchange resin and the column was eluted with water and then methanol. From the first fraction (80 cc. of aqueous elute), 0.7 g. of crystalline material, m. p. 198°C with decomposition was obtained. Subsequently, following fractions were discarded. It liberated iodine from acid solution of potassium iodide. From this fact, it seems to contain hydrogen peroxide of crystallization[4,7]. Recrystallization from methanol gave 0.2 g. of *N*-oxide-b which showed m. p. 205°C (decomp.)*. It was slightly soluble in chloroform and insoluble in ethyl acetate. The specimen several months old had lost hydrogen peroxide, and it showed no diminution of its weight by drying in vacuo at 100~110°C. It melted at 209°C with decomposition. The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (3.15 μ), an acetoxyl group (5.82 and 8.09 μ), an *N*-oxide group (10.47 μ) and a terminal methylene group (11.07 μ).

Found: C, 69.32; H, 8.27. Calcd. for $C_{24}H_{35}O_5N$: C, 69.03; H, 8.45%.

Reduction of Lucidusculine *N*-Oxide.—The *N*-oxide-b (0.15 g.) freshly prepared from lucidusculine by perbenzoic acid oxidation for 2 days was dissolved in 1.5 cc. of 10% sulfuric acid**. To this solution, a drop of cupper sulfate solution was added and then 0.15 g. of zinc powder was gradually added. After standing for 2.5 hr. the reaction mixture was filtered, made alkaline with aqueous ammonia and extracted with chloroform. After removal of the chloroform, the residue was crystallized from methanol. It melted at 169~173°C and showed no depression of the melting point on admixture with lucidusculine.

Oxidation of Lucidusculine with *N*-Bromosuccinimide [Dehydrolucidusculine (V)].—Lucidusculine (0.5 g.) and *N*-bromosuccinimide (0.23 g.) were dissolved in 250 cc. of benzene. After boiling for 3 hr., the formed precipitate was removed by filtration. The filtrate was evaporated to dryness in vacuo. The residue dissolved in chloroform was washed three times with sodium carbonate solution and then three times with water. After removal of the chloroform, the residue was redissolved in chloroform and chromatographed on alumina. The chromatogram was eluted with chloroform and acetone and then methanol. From the chloroform portion (15 cc.), 50 mg. of residue was obtained, which on recrystallization from methanol, melted at 175~180°C. From the acetone portion (30 cc.), impure lucidusculine was obtained. Accordingly, the methanol portion (15 cc.) was discarded. The ultraviolet absorption spectrum of this compound (m. p. 175~180°C) showed end absorption and no maximum. The infrared absorption spectrum in Nujol showed the presence of a hydroxyl group (3.08 μ), an acetoxyl group (5.76 and 8.09 μ), a terminal methylene group (10.75 μ) and a carbinolamine ether (10.15 and 11.34 μ).

Found: C, 71.51; H, 8.41. Calcd. for $C_{24}H_{33}O_4N$: C, 72.15; H, 8.33%.

Dehydrolucidusculine (V) from Lucidusculine *N*-Oxide.—To 76 cc. of 1% K_2CrO_4 solution, was added lucidusculine *N*-oxide (200 mg.), which was the same sample as that used for the above described reduction. The material was heated on a water bath. The solution, which was transparent at first, became turbid in about thirty minutes. After heating for 1.5 hr., the separated material (50 mg.) was collected by filtration. It was dissolved in chloroform and the filtered solution was concentrated. On addition of methanol, a crystalline substance was obtained. On recrystallization from acetone, it melted at 173~177°C and showed no depression on admixture with sample obtained by the above described NBS oxidation.

Found: C, 72.38; H, 8.74***. Calcd. for $C_{24}H_{33}O_4N$: C, 72.15; H, 8.33%.

Bromoanhydrolucidusculine Hydrobromide (VI).—To a solution of lucidusculine (0.5 g.) dissolved in 10 cc. of methanol, a freshly prepared 0.25 M solution of bromine in methanol was added dropwise. Excessive bromine was detected by potassium iodide starch paper. In total 8.5 cc. of reagent were added; after one hour, excessive bromine persisted (1 mol. 5.07 cc.). When the methanol solution was concentrated, it showed acid reaction to Congo red. It was evaporated to dryness in vacuo. The residue, on recrystallization from methanol, gave crystals, m. p. 210°C (decomp.). $[\alpha]_D^{15}$ −64.63°C (methanol). The ultraviolet absorption spectrum of this compound in methanol is graphed in Fig. 1. The infrared absorption spectrum in Nujol had no band attributable to a terminal methylene group; it showed the presence of a hydroxyl group (2.99 μ), an acetoxyl group (5.78 and 8.16 μ) and water (6.05 μ).

Found: C, 50.02; H, 6.74; Br, 29.70; H_2O, 5.5. Calcd. for $C_{24}H_{32}O_4NBr \cdot HBr \cdot 2H_2O$: C, 49.73; H, 6.43; Br, 27.57; H_2O, 6.2%.

The hydrobromide was soluble in water. The base, liberated from the hydrobromide with aqueous ammonia, could not have been obtained in a crystalline form on treatment with methanol.

The Amino Acid (VII).—A mixture of lucidusculine (1.8 g.) and chromium trioxide (2.4 g.) in

* This material seems to be purer than the *N*-oxide-b which showed m. p. 200°C (decomp.).

** For hydrochloric acid[1], 10% sulfuric acid is substituted.

*** The figure, 8.75[1], was misprinted.

pyridine (48 cc.) that had been allowed to stand at room temperature overnight was filtered. The filtrate was evaporated to dryness in vacuo. The residue was treated with water saturated with sulfur dioxide. After standing overnight, the acid solution was made alkaline with saturated baryta water to precipitate chromic hydroxide. The alkaline solution from which the precipitate had been removed by filtration was made slightly acid by the addition of 10% sulfuric acid, and the precipitated barium sulfate was removed. The concentrated filtrate was neutralized with baryta water and was evaporated to dryness. The residue was treated with methanol and the undissolved barium sulfate was removed by filtration. The methanol solution was evaporated to dryness. To a solution of the residue (1.8 g.) dissolved in 9.5 cc. of methanol, 34 cc. of acetone was added. Then a yellow precipitate was formed. The transparent solution separated from the precipitate was concentrated to obtain a crystalline material; it weighed 1.4 g. It was dissolved in methanol (5.5 cc.). Upon the addition of 28 cc. of ethanol, 0.3 g. of a crystalline material was obtained. The mother liquor gave a second crop (0.3 g.) on recrystallization from methanol-ethanol.

The combined crystalline material (0.6 g.) was dissolved in 30 cc. of 70% methanol. The solution was passed through a column of 10 cc. of cation-exchange resin (Dowex 50) and eluted with the same solvent. The elute (280 cc.) was evaporated to dryness and yielded 540 mg. of crystalline residue. It was recrystallized from 70% methanol and gave 200 mg. of pure material. It was soluble in water and methanol but not in ethanol and other organic solvents. It showed no definite m. p. nor d. p. and gradually became black above 350°C. $[\alpha]_D^{16}$ −26.22° (methanol). The ultraviolet absorption spectrum of this compond in methanol is graphed in Fig. 1. The infrared absorption spectrum in Nujol showed the presence of hydroxyl groups (2.92 μ), an acetoxyl group (5.78 and 8.11 μ), a ketone carbonyl group (5.85 μ), water (6.06 μ) and an ionized carboxyl group (6.19 μ).

Found: C, 54.22, 54.60; H, 7.88, 7.69; N, 3.05; H_2O, 10.11. Calcd. for $C_{24}H_{33}O_9N \cdot 3H_2O$[26]: C, 54.02; H, 7.36; N, 2.62; H_2O, 10.12%.

The Methyl Ester (VIII).—To the amino acid (0.25 g.) dissolved in methanol (12.5 cc.), a slight excess of ethereal solution of diazomethane was added. The reaction mixture was allowed to stand overnight and then was evaporated to dryness. The residue was dissolved in 1 N HCl and was precipitated by the addition of aqueous ammonia. The precipitate (0.1 g.) was crystallized from methanol-ethyl acetate and was further recrystallized from methanol. It showed no definite melting point nor definite d. p. and it swelled gradually with decomposition near 288°C. The ultraviolet absorption spectrum of this compound in methanol showed end absorption and no maximum.

Found: C, 57.01; H, 7.70; H_2O, 6.01. Calcd. for $C_{25}H_{35}O_9N \cdot 2H_2O$[26]: C, 56.69; H, 7.42; H_2O, 6.80%.

26) From the result of determination of water of crystallization the previously reported molecular formula[1] is revised to this.

Summary

The alkaloid lucidusculine was oxidized by hydrogen peroxide and also by perbenzoic acid to lucidusculine *N*-oxide. The *N*-oxide could be converted back into the original base by reduction. Oxidation of the alkaloid with *N*-bromosuccinimide afforded dehydrolucidusculine which was also produced by transformation of lucidusculine *N*-oxide. Dehydrolucidusculine seems to be a cyclic carbinolamine internal ether. The action of bromine on the alkaloid was noticeable and gave bromoanhydrolucidusculine hydrobromide which was probably obtained from the intermediate dibromide with loss of one mole each of water and hydrogen bromide. Chromium trioxide-pyridine complex oxidized lucidusculine to an amino acid which, on methylation with diazomethane, gave a methyl ester. From these experimental results, the previously proposed partial formula of lucidusculine was further extended.

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Untersuchungen über Meso-ionischen Verbindungen. X[1] *Synthesen von 4-Substituierten 3-(β-Pyridyl)sydnonen*

Von Masaki OHTA und Mitsuo MASAKI

(Engegangen am 16 Oktober, 1959)

N-Pyridylglycin, das in der Synthese von 3-(β-Pyridyl)sydnon eine Zwischenverbindung ist, kann nicht durch die gewöhnlichen Reaktionen, z. B. durch die Reaktion von β-Aminopyridin mit Chloressigsäure, gewonnen werden, sondern nur durch Reduktivkondensation von β-Aminopyridin und Glyoxylsäureäthylester im Autoklaven, wie es schon berichtet worden ist[2]. Bisher ist kein 4-substituiertes 3-(β-Pyridyl)sydnon erhalten worden.

Nach der Umsetzungsmethode von Amin über Aminoacetonitril in Aminoessigsäure, die von Knoevenagel[3], Tiemann[4], Bristow[5], u. a. beschrieben worden sind, haben wir *N*-(β-Pyridyl)-*N*-nitrosoglycin (IV-a), *N*-(β-Pyridyl)-*N*-nitroso-α-methylglycin (IV-b), und *N*-(β-Pyridyl)-*N*-nitroso-α-phenylglycin (IV-c) gewonnen, und diese drei *N*-Nitrosoglycine setzen sich durch Erwärmen mit Acetanhydrid in die entsprechenden Meso-ionischen Verbindungen um.

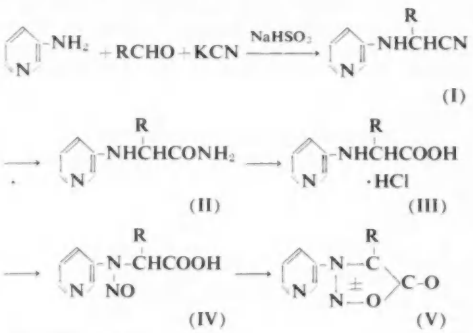
Wir stellten so 3-(β-Pyridyl)sydnon (V-a), 3-(β-Pyridyl)-4-methylsydnon (V-b) und 3-(β-Pyridyl)-4-phenylsydnon (V-c) dar.

In Wasser als Lösungsmittel reagiert β-Aminopyridin mit Bisulfitverbindung des Formaldehyds und Alkalicyanids, und β-Pyridylaminoacetonitril (I-a) wird erhalten, das durch Erhitzen im Reaktiongemisch β-Pyridylaminoacetamid (II-a) liefert, aus dem durch Hydrolyse mit Alkali oder Säure *N*-(β-Pyridyl)glycin zugänglich ist.

Das Glycin wurde durch sein Salzsäuresalz (III-a) festgestellt. Man kann aber das *N*-Nitrosoglycin unmittelbar durch das Zusetzen des Natriumnitrits zu der salzsäuresaueren wässerigen Lösung von Glycin gewinnen, nachdem man das Amid in Alkalilösung erwärmt hat. Das *N*-Nitrosoglycin liefert phototropisches Sydnon, wenn man es mit Acetanhydrid erwärmt, wie J. M. Tien u. a.[2] beschrieben haben.

Ganz analog reagiert β-Aminopyridin mit Bisulfitverbindung des Acetaldehyds oder des Benzaldehyds und Alkalicyanid, wobei α-(β-Pyridylamino)propionitril (I-b) oder α-(β-Pyridylamino)-phenylacetnitril (I-c) entsteht, das sich in das entsprechende Amid durch Auflösen in konz. Schwefelsäure überführen läßt.

Durch das Erhitzen mit Salzsäure läßt sich α-(β-Pyridylamino)phenylacetamid (II-c) in das salzsauere α-(β-Pyridylamino)phenylglycin (III-c) verseifen. Nur α-(β-Pyridylamino)-propionamid (II-b) zersetzt sich bei Erwärmen mit konzentrierter oder verdünnter Salzsäure in braunrotes Öl* und Ammoniumchlorid.



(I) (II) (III) (IV) (V)

-R = -H : a)
-R = -CH_3 : b)
-R = -C_6H_5 : c)

Die beiden Amide sind aber am besten durch das mehrstündige Erwärmen mit Alkali in die entsprechende Säure unzuwandeln. Wenn man die erhaltenen Lösungen mit Salzsäure und Natriumnitrit unter Kühlen versetzt, so entstehen die entsprechenden *N*-Nitrosoglycine, aus denen durch Dehydratisierung die zwei 4-substituierten 3-(β-Pyridyl)sydnone zugänglich sind. Sie zeigen sich aber nicht phototropisch.

Beschreibung der Versuche

3-(β-Pyridyl)sydnon (V-a).—*β-Pyridylaminoacetonitril (I-a).*—Man versetzt 41 g von etwa 37% Formaldehydlösung mit 13.2 g von ca. 40% Natriumbisulfitlösung und darauf mit 4.7 g β-Aminopyridin. Das Gemisch wurde auf dem Wasserbad eine Std. erwärmt, dann setzt man 4 g Natriumcyanid in konzentrierter, wässeriger Lösung zu. Nach einigem Stehen scheidet sich ein Öl ab, das 2~3 mal mit Chloroform ausgeschüttelt wird. Das nach dem

1) IX. Mitteil. : H. Kato und M. Ohta, Dieses Bulletin, 32, 282 (1959).
2) J. M. Tien und I. M. Hunsberger, *J. Am. Chem. Soc.*, 77, 4604 (1955).
3) E. Knoevenagel *Ber.*, 37, 4073 (1904). E. Knovenagel und Merkin, ebenda, 37, 4090 (1904).
4) F. Tieman und R. Stephan, ebenda, 15, 2028 (1882). F. Tieman u. a., ebenda, 15, 2034 (1882).
5) N. W. Bristow, *J. Chem. Soc.*, 1954, 616.

* Diese Reaktion untersuchen wir noch jetzt.

Abdampfen des Chloroforms zurückgebliebene Nitril wird aus Chloroform umkristallisiert. Farblose Nadeln vom Schmp. 77°C. Ausb. 4.9 g (74% d. Th.)

$C_7H_7N_3$

Ber. N 31.56
Gef. N 31.69

β-Pyridylaminoacetamid (II-a). — Ohne Extrahierung mit Chloroform erhitzt man das Nitril in dem oben erhaltenen Reaktionsgemisch auf dem siedenden Wasserbad noch 2~3 Stdn. Das abgeschiedene Öl läßt sich wieder lösen und die Lösung färbt sich braunschwarz, woraus sich beim Erkalten derbe Prismen abscheiden, und dann werden sie abfiltriert und aus dem Wasser umkristallisiert. Farblose derbe Nadeln vom Schmp. 166°C. Ausb. 4.7 g. (63% d. Th.)

$C_7H_9N_3O$

Ber. C 55.61 H 6.00 N 27.80
Gef. C 55.23 H 6.23 N 28.04

Salzsaures N-(β-Pyridyl)glycin (III-a).—Man löst 1.5 g β-Pyridylaminoacetamid in einer Mischung von 5 ccm konz. Salzsäure und 3 ccm Äthanol, und erhitzt dieses auf einem Wasserbad 3~4 Stdn. Der beim Erkalten abgeschiedene, farblose Niederschlag, Ammoniumchloride, wurde abfiltriert. Das Filtrat trocknet man durch Eindampfen unter vermindertem Druck, und die zurückgebliebene Kristallmaße kristallisiert sich aus konz. Salzsäure in farblose Prismen vom Schmp. 222~224°C. Ausb. 1.3 g (72% d. Th.).

$C_7H_9N_2O_2Cl$

Ber. N 14.85
Gef. N 14.80

In 14 ccm Wasser löst man 1.3 g. β-Pyridylaminoacetnitril, setzt 0.69 g. K_2CO_3 und 0.28 g. CaO zu, und dann wird es 4 Stdn. lang gelinde, unter Anwendung eines Asbestdrahtnetzes erhitzt. Wenn die Entwicklung von Ammoniak aufgehört hat, so kühlt man diese Lösung. Man filtriert den gebildeten farblosen Niederschlag, $CaCO_3$, ab, sättigt dann das Filtrat mit Chlorwasserstoff unter Kühlung, fügt etwa 15 ccm Äthanol hinzu und sätfigt wieder die Flüssigkeit mit Chlorwasserstoff. Der abgeschiedene Niederschlag, KCl, läßt sich abfiltrieren und das Filtrat wird durch Eindampfen im Vakuum getrocknet, wobei salzsaueres *N*-(β-Pyridyl)glycin hinterbleibt.

N-Nitroso-N-(β-pyridyl)glycin (IV-a). — Man löst 1.5 g NaOH in 40 ccm Wasser auf, versetzt mit 5.0 g β-Pyridylaminoacetamid, und erwärmt es 5~6 Stdn. unter mechanischem Rühren auf 40~50°C. Hierauf kühlt man die Lösung auf 0°C ab, fügt langsam 7.1 g konz. Salzsäure hinzu, und versetzt dann diese Lösung mit 2.5 g Natriumnitrit, wobei die Temperatur nicht über +1°C steigen soll. Nach einigem Stehen scheidet sich ein farbloser Niederschlag ab, der bei 158°C schmilzt. Die Mischprobe mit dem durch das Verfahren von J. M. Tien[2] erhaltenen *N*-Nitroso-*N*-(β-pyridyl)glycin, zeigt keine Schmelzpunkterniederung.

3-(β-Pyridyl)sydnon (V-a).—Eine Mischung von 1.5 g (IV-a) und 20 ccm Essigsäureanhydrid wird auf siedendem Wasserbad erhitzt. Nach einer halben Stunde wird die Lösung unter vermindertem Druck in N_2 eingeengt, wobei 3-(β-Pyridyl)sydnon sich abscheidet. Die aus dem Wasser umkristallisierten, farblosen Prismen vom Schmp. 119~121°C sind eine photropische Verbindung.

3-(β-Pyridyl)-4-methylsydnon (V-b). — *α-(β-Pyridyl)aminopropionitril (I-b).*—Man versetzt 26.4 g von etwa 40 proz. Natriumbisulfitlösung mit 10 g von 44 proz. Acetaldehyd und dann mit 9.4 g β-Aminopyridin. Zuerst eine halbe Stunde lang bei Raumtemperatur, darauf rührt man eine Stunde lang in einem Wagserbad von 80°C die Mischung um, und nach dam Abkühlen bis zur Raumtemperatur setzt man dazu 6.5 g Kaliumcyanid in wenigem wasser zu. Nach einigem Stehen scheidet sich ein Öl ab. 4~5 Stdn. lang rührt man das Gemisch bei Raumtemperatur um, darauf schüttelt man es 6~7 mal mit Chloroform aus, trocknet die vereinigten Chloroformextrakte mit Natriumsulfat und dampft im Vakuum ein. Es hinterbleiben 8 g α-(β-Pyridyl)-aminopropionitril (Ausb. 54% d. Th.) die zur Analyse 2 mal mit Äther gewaschen werden. Farblose Nadeln vom Schmp. 98~100°C.

$C_8H_9N_3$

Ber. N 28.55
Gef. N 28.50

α-(β-Pyridyl)aminopropionamid (II-b).—Man fügt 8 g (I-b) zu 60 g konz. Schwefelsäure unter Umrühren nach und nach hinzu, wobei die Temperatnr nicht über 5°C steigen soll. Nach 4~5 Stdn. Umrühren läßt man die schwefelsäure Lösung einen Tag bei Raumtemperatur stehen, gießt die klare Lösung in 200 g zerstoßenes Eis und versetzt diese mit Ammoniak bis zur neutralen Reaktion. Der nach einigem Stehen abgeschiedene Niederschlag wird abfiltriert und aus Äthanol umkristallisiert. Farblose Prismen vom Schmp. 179°C. Ausb. 6.8 g (76% d. Th.).

$C_8H_{11}N_3O$

Ber. N 25.44
Gef. N 25.84

N-Nitroso-N-(β-pyidyl)methylglycin (IV-b).—Eine Mischung von 2 g des fein pulverisierten Amids und 16 ccm ca. 4 proz. Natronlauge ist solange umzurühren und auf einem Wasserbad von 40~50°C zu erwärmen, bis das Amid ganz in Auflösung übergegangen ist. Nach 9~10 Stdn. fügt man unter Kühlung 3 ccm konz. Salzsäure vorsichtig hinzu, und versetzt mit 1 g Natriumnitrit, wobei die Temperatur unter 0°C zu behalten ist. Bald scheidet sich ein Niederschlag ab, der nach einer Stunde abfiltriert wird und den man, wenn notwendig, aus dem Wasser umkristallisieren kann. Farblose Prismen vom Schmp. 135°C. Ausb. 2.2 g (92% d. Th.).

$C_8H_9N_3O_3$

Ber. N 21.53
Gef. N 21.50

3-(β-Pyridyl)-4-methylsydnon (V-b).—Man löst 1.7 g (IV-b) in 20 ccm Essigsäureanhydrid durch Erhitzen auf siedendem Wasserbad anf. Nach einer Viertelstunde wird die Lösung unter vermindertem Druck in N_2 abgedampft. Es hinterbleibt 1 g 3-(β-Pyridyl)-4-methylsydnon, das mit verdünntem Alkohol gewaschen wird. Aus Wasser umkristallisiert zeigen farblose schuppige Kristalle den Schmp. 143°C. Ausb. 70% d. Th.

$C_8H_7N_3O_2$
Ber. C 54.23 H 3.98 N 23.72
Gef. C 53.98 H 4.26 N 23.83

3-(β-Pyridyl)-4-phenylsydnon (V-c). — *α-Phenyl-(β-pyridylamino)acetonitril (I-c).*—Man schüttelt 15 g Benzaldehyd mit 41 g ca. 40% Natriumbisulfitlösung, und der erhaltene Kristallbrei wird mit 15 g β-Aminopyridin versetzt. Dann erwärmt man das Gemisch auf dem Wasserbad solange, bis die wässerige Reaktionsmischung vollständig verflüssigt und klar wird. Dann setzt man 11 g Kaliumcyanid, in wenigem Wasser gelöst, zu. Nach ungefähr 2~3 Stdn. Umrühren wird der gebildete Niederschlag abfiltriert, mit Äther gut gewaschen und aus siedendem Äthanol umkristallisiert. Rotgelbliche Prismen vom Schmp. 117°C. Ausb. 24 g (76% d. Th.).

$C_{13}H_{11}N_3$
Ber. N 20.08
Gef. N 20.19

α-Phenyl-(β-pyridylamino)acetamid (II-c).—Zu 160 g konz. Schwefelsäure fügt man 24 g (I-c) unter Kühlung allmählich hinzu, hierbei ist das Gemisch solange umzurühren, bis Nitril völlig in Auflösung gegangen ist. Bei Raumtemperatur läßt man die klare Lösung einen Tag stehen, gießt sie dann in 300 g zerstoßenes Eis, und neutralisiert darauf vorsichtig mit Ammoniak, wobei α-Phenyl-(β-pyridylamino)acetamid sich als ein gelblicher Niederschlag ausscheidet. Aus Äthanol umkristallisiert, erzeugen sich farblose Nädelchen vom Schmp. 191°C. Ausb. 5.2 g (26% d. Th.).

$C_{13}H_{13}N_3O$
Ber. N 18.49
Gef. N 18.44

Salzsaures α-Phenyl-(β-pyridylamino)essigsäure (III-c).—Man löst 2 g (II-c) in 18 ccm konz. Salzsäure und erhitzt dies 4~5 Stdn. auf siedendem Wasserbad. Das gebildete Ammoniumchlorid filtriert man ab, und dampft das Filtrat bis zum Trocknen im Vakuum ein. Der Rückstand wird 2~3 mal aus konz. Salzsäure umkristallisiert. Farblose Prismen vom Schmp. 218~220°C. Ausb. 1.7 g (73% d. Th.).

$C_{13}H_{13}O_2N_2Cl$
Ber. N 10.59
Gef. N 10.67

N-Nitroso-N-(β-pyridyl)phenylglycin (IV-c). — (1) In 7 ccm Wasser wird 1 g salzsaures *N*-(β-Pyridyl)-phenylglycin gelöst und dann dazu 0.3 g $NaNO_2$ hinzugefügt, wobei die Temperatur unter 0°C bleiben soll. Nach einigem Stehen wird der gebildete, farblose Niederschlag abfiltriert, der bei 147°C schmilzt und zur Analyse vollständig rein ist. Ausb. 0.8 g (84% d. Th.).

$C_{13}H_{11}N_3O_3$
Ber. N 16.34
Gef. N 16.35

(2) Eine Mischung von 5.2 g (II-c) und 40 ccm ca. 2.5 proz. Natronlauge wird unter mechanischem Rühren auf einem Wasserbad von 70~80°C solange erwärmt, bis das Amid vollständig aufgelöst ist. Zur, nach 5~6 Stdn. erhaltenen, klaren, wässerigen Lösung fügt man 5 ccm konz. Salzräure hinzu und versetzt darauf das Gemisch mit 1.9 g Natriumnitrit, wobei die Temperatur nicht über 0°C steigen soll. Der bald ausgefallene Niederschlag schmilzt bei 147°C, und zeigt bei der Mischprobe mit der aus Glycin hergestellten Verbindung keine Schmelzpunkterniederung. 4.5 g (76% d. Th.).

3-(β-Pyridyl)-4-phenylsydnon (V-c).—Man fügt 4.7 g (IV-c) zu 40 ccm Essigsäureanhydrid hinzu, und erhitzt es 20 minutenlang auf siedendem Wasserbad. Die erhaltene, klare, braune Lösung wird unter vermindertem Druck in N_2 eingedampft, wobei 3.7 g Rückstand hinterbleibt, der mit ein wenig verd. Alkohol gewaschen wird. Die aus verd. Äthanol umkristallisierte, gelbliche Nadeln zeigen den Schmp. 118~120°C. Ausb. 3.1 g (70% d. Th.).

$C_{13}H_9N_3O_2$
Ber. C 65.26 H 3.79 N 17.57
Gef. C 64.85 H 3.94 N 17.59

Herrn Asaji Kondo danken wir bestens für seine Ausführung der Mikro-analyse.

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Hydrogen Abstraction from Hydrogen Sulfide Molecules by Methyl Radicals

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A study of the hydrogen sulfide catalyzed thermal decomposition of acetaldehyde carried out in this laboratory suggested that the catalysis is at least in part ascribed to hydrosulfide radicals produced by the reaction of methyl radicals with hydrogen sulfide molecules. It seemed then desirable to investigate this hydrogen abstraction reaction quantitatively, for only limited information was available on this reaction.

The technique used in this work is one of the competitive methods which have frequently been applied to study reactions of free radicals: acetone vapor has been photolyzed in the presence of varied amounts of hydrogen sulfide; the analysis of the products has yielded the ratio of the rate of the abstraction reaction in question to that of the recombination reaction of methyl radicals; the rate of the former reaction can then be estimated since that of the latter has already been the subject of a number of extensive investigations.

Experimental

Materials.—Acetone used in this experiment was supplied commercially and purified by bulb-to-bulb distillation. Hydrogen sulfide was prepared by dropping water on aluminium sulfide in a vacuum system, dried by passing through a trap at $-78°C$ and purified by bulb-to-bulb distillation. Cupric oxide and cupric sulfate used in analyses were commercial samples.

Apparatus.—Photolysis was carried out in a cylindrical quarz vessel of about 110 cc. capacity placed in an electric furnace with a glass window which cuts off the light of a wave length shorter than 2800 Å. Therefore, no light was absorbed by hydrogen sulfide. The reaction vessel was connected to a mercury manometer, to an analytical system, and to a capillary tube of small volume, which had a mercury manometer and was used to measure a small quantity of hydrogen sulfide to be admitted to the vessel. The full light from a medium-pressure mercury arc was used in the present experiment. In order to increase light intensity it was placed at a focus of a half spheroidal mirror and at the other focus the center of the vessel was placed. Light intensity was kept constant by using a voltage stabilizer. The vessel, manometer, storage bulbs and the analytical system were attached to a conventional vacuum line.

Procedure.—A small measured quantity of hydrogen sulfide was admitted to the reaction vessel. Acetone vapor with a desired pressure was then added. After a few minutes to allow the gases to mix thoroughly and to come to a desired temperature, light was admitted into the vessel and irradiation was continued for a desired time.

Analysis.—After the photolysis, using a Toepler gauge, the reactants and products were passed through a trap at $-78°C$ where the unreacted acetone and low boiling point products were condensed. The uncondensable fraction at $-78°C$ was passed through a trap at $-196°C$ and the quantity of uncondensable fraction at $-196°C$ was measured by Toepler gauge. This fraction contained methane and carbon monoxide and was passed over cupric oxide at $250°C$ where carbon monoxide was oxidized to carbon dioxide and hydrogen, if any, to water. By the Toepler gauge these gases were passed through a trap at $-78°C$ where water, if any, was condensed, and through another one at $-196°C$ where carbon dioxide was condensed. The uncondensable fraction contained only methane, and its quantity was measured by the Toepler gauge. The condensed carbon dioxide was vaporized at room temperature and its quantity was measured by a McLeod gauge connected with the trap. The quantity of product uncondensable at $-196°C$ was always equal to the sum of quantities of methane and carbon monoxide analyzed within an error of 1%. That no water was found in all the runs showed that no hydrogen was formed in the photolysis. The fraction uncondensable at $-78°C$ and condensable at $-196°C$ contained the remaining hydrogen sulfide, ethane and other products. This fraction was vaporized and led to a trap at $-196°C$ through another one at about $-160°C$. The uncondensable fraction at $-160°C$ was vaporized and measured by the McLeod gauge. This fraction should have contained only hydrogen sulfide and ethane. Hydrogen sulfide was removed by contact with dry cupric sulfate. Thus the quantities of ethane and hydrogen sulfide were determined separately.

Results and Discussion

A series of preliminary experiments with varied times of irradiation under otherwise constant conditions revealed that all the rates of formation of carbon monoxide, methane and ethane remain nearly constant at least during the initial stage of the photolysis up to about 0.2% conversion, which justifies the computation of initial rates of formation of these products from the analytical results at such low

TABLE I. THE EFFECT OF HYDROGEN SULFIDE ON THE PHOTOLYSIS OF ACETONE

Temp. °C	Initial concentration mol. cc^{-1}		Time sec.	Rate of formation mol. cc^{-1} sec^{-1}			$R_{CH_4}/R_{C_2H_6}^{1/2}$ $\times 10^6$
	$[Acetone]_0$ $\times 10^6$	$[H_2S]_0$ $\times 10^9$		R_{CO} $\times 10^{12}$	R_{CH_4} $\times 10^{12}$	$R_{C_2H_6}$ $\times 10^{12}$	
50	3.87	0	3000	6.01	0.968	6.52	0.38
	3.92	0	2000	6.00	1.05	6.45	0.41
	3.85	3.02	200	9.2	6.5	5.25	2.84
	3.90	4.22	300	6.73	8.17	3.81	4.27
	3.89	4.9	300	9.1	9.0	3.77	4.64
	3.89	5.3	300	7.23	9.1	3.30	5.00
	3.86	8.2	400	5.74	11.1	2.00	7.88
	3.89	9.9	500	5.40	12.5	1.80	9.33
90	3.92	0	3000	20.6	3.28	18.6	0.752
	3.87	0	1000	25.4	3.77	21.0	0.823
	3.90	1.57	100	24.3	12.2	15.2	3.13
	3.87	2.48	100	24.8	15.9	13.7	4.30
	3.90	3.65	100	25.0	18.3	10.7	5.6
	3.90	5.0	200	22.0	21.7	7.75	7.8
	3.87	6.3	200	22.0	24.2	7.62	8.8
	3.89	9.5	200	22.5	27.3	5.12	12.1
	6.94	0	2000	29.3	6.80	22.5	1.43
	6.92	2.83	100	39.3	22.6	21.5	1.89
	6.93	4.2	200	37.5	28.2	18.4	6.57
	6.91	6.0	100	37.0	34.9	13.5	9.51
	6.90	9.1	200	30.6	37.3	6.64	14.4
	6.88	11.3	200	28.0	38.8	5.57	16.5
140	3.88	0	3000	39.3	15.0	29.0	2.79
	3.88	0	3600	41.8	15.1	28.0	2.85
	3.88	1.70	100	35.2	25.4	14.5	6.06
	3.89	3.80	100	33.9	31.6	8.60	10.8
	3.87	4.75	100	31.0	32.0	6.60	12.4
	3.88	6.5	200	30.0	35.4	4.62	16.5
	3.88	8.5	200	29.0	36.8	3.33	20.2
200	3.85	0	1000	41.2	34.2	11.0	10.3
	3.39	0	2000	22.3	22.0	5.20	9.4

conversions[1]. In Table I are listed the initial rates of formation of these products thus determined in several series of experiments. Within a series only the initial concentration of hydrogen sulfide was varied to determine the dependence of the rate on its concentration. The intensity of light was kept nearly constant throughout all the runs. As the concentration of hydrogen sulfide was increased, the rate of formation of ethane was decreased as seen in the table. On the other hand, use of too much hydrogen sulfide made its removal by dry cupric sulfate in analysis incomplete so that the rate of ethane formation was then liable to be overestimated. This situation limited the concentration range for hydrogen sulfide to those given in Table I.

It has been established[2-5] that during the photolysis of acetone, metane, ethane and carbon monoxide are produced almost entirely by the following reactions:

$$CH_3COCH_3 + h\nu = CH_3CO + CH_3 \quad (1)$$

$$CH_3CO = CH_3 + CO \quad (2)$$

$$CH_3 + CH_3 = C_2H_6 \quad (3)$$

$$CH_3 + CH_3COCH_3 = CH_4 + CH_3COCH_2 \quad (4)$$

1) It was found in the present work that the hydrogen sulfide initially added is consumed as the photolysis is continued. The ultimate fate of the hydrogen sulfide will be dealt with in a later paper.

2) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, **9**, 616 (1941).

3) A. F. Trotman-Dickenson and E. W. R. Steasie, ibid., **18**, 1097 (1950).

4) R. Gomer and G. B. Kistiakowsky, ibid., **19**, 851 (1951).

5) M. T. Jaquiss, J. S. Roberts and M. Szwarc, *J. Am. Chem. Soc.*, **74**, 6005 (1952).

Reactions 3 and 4 lead to the following equation

$$R_{CH_4}/R_{C_2H_6}{}^{1/2} = (k_4/k_3{}^{1/2})\,[CH_3COCH_3] \quad (I)$$

which is in agreement with experimental results. In the presence of hydrogen sulfide, the reaction

$$CH_3 + H_2S = CH_4 + HS \quad (5)$$

may occur[6] and reactions 3, 4 and 5 taken together now yield

$$R_{CH_4}/R_{C_2H_6}{}^{1/2} = (k_4/k_3{}^{1/2})\,[CH_3COCH_3] + (k_5/k_3{}^{1/2})\,[H_2S] \quad (II)$$

When the concentration of acetone is kept constant, the plot of $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ vs. $[H_2S]$ should give a straight line, and its intercept should be equal to the value of $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ in the absence of hydrogen sulfide. Fig. 1 shows such plots of the results given in Table I and it is seen that the above requirements are in fact satisfied. That the slope of the straight line is not affected by a two-fold increase in the acetone concentration at 90°C may be taken as additional evidence for the validity of Eq. II. From the slopes of these straight lines, values of $k_5/k_3{}^{1/2}$ at various temperatures were determined and are shown in Table II together with those of $k_4/k_3{}^{1/2}$ obtained in the absence of hydrogen sulfide.

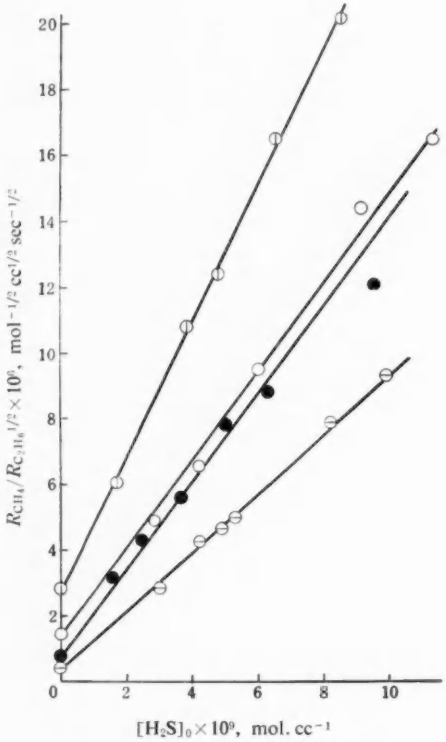

Fig. 1. Dependence of the ratio $R_{CH_4}/R_{C_2H_6}{}^{1/2}$ on the concentration of hydrogen sulfide.
⊖, $[Acetone]_0 = 3.9 \times 10^{-6}$ mol. cc^{-1}, 50°C;
●, $[Acetone]_0 = 3.9 \times 10^{-6}$ mol. cc^{-1}, 90°C;
○, $[Acetone]_0 = 6.9 \times 10^{-6}$ mol. cc^{-1}, 90°C;
◐, $[Acetone]_0 = 3.9 \times 10^{-6}$ mol. cc^{-1}, 140°C.

TABLE II. VALUES OF $k_5/k_3{}^{1/2}$ AND $k_4/k_3{}^{1/2}$

Temp. °C	$k_5/k_3{}^{1/2}$ mol$^{-1/2}$ cc$^{1/2}$ sec$^{-1/2}$	$k_4/k_3{}^{1/2}$ mol$^{-1/2}$ cc$^{1/2}$ sec$^{-1/2}$
50	880	0.102
90	1350	0.210
140	2080	0.727
200	—	2.71

The Arrhenius plot of $k_4/k_3{}^{1/2}$ shows a cutvature at temperatures below 100°C as is well known. According to Ausloos and Steacie[7] this falling off in the apparent activation energy at low temperatures presumably arises from a reaction between methyl radicals and adsorbed acetone molecules on the wall and a disproportionation reaction between methyl radicals and acetyl radicals. The excessive value of $k_4/k_3{}^{1/2}$ in question, however, caused no more than 3% error in the value of $k_5/k_3{}^{1/2}$ even at 50°C. The values of $k_4/k_3{}^{1/2}$ at 140° and 200°C are in satisfactory agreement with those previously reported[2-5].

In contrast, the Arrhenius plot of $k_5/k_3{}^{1/2}$ yielded a good straight line from which $E_5 - 1/2E_3 = 2.6$ kcal. mol^{-1} and $A_5/A_3{}^{1/2} = 10^{4.675}$ mol$^{-1/2}$ cc$^{1/2}$ sec$^{-1/2}$ are obtained, where E denotes the activation energy and A the pre-exponential factor. Accepting the values $E_3 = 0$ and $A_3 = 10^{13.35}$ mol^{-1} cc. sec^{-1} as recommended by Shepp[8] we find

$$k_5 = 10^{11.4} \exp(-2{,}600/RT) \text{ mol}^{-1} \text{ cc. sec}^{-1}$$

The value of $A_5 = 10^{11.4}$ mol^{-1} cc. sec^{-1} seems to be reasonable, since most A factors for hydrogen abstraction reactions by methyl radicals are of the order of 10^{11} mol^{-1} cc. sec^{-1}.

On the other hand, the value of $E_5 = 2.6$ kcal. mol^{-1} might be regarded unexpectedly low. Birrell, Smith, Trotman-Dickenson and Wilkie[9] have reported that the apparent order of reactivities of thiols towards methyl radical are given by

$$Bu^tSH > Pr^iSH > EtSH > MeSH > H_2S$$

6) Subsequent reactions of hydrosulfide radicals formed by reaction 5 are under investigation. There is, however, little indication that these reactions affect the importance of reaction 3 in forming ethane and that any other important source of methane besides reactions 4 and 5 must be considerd.

7) P. Ausloos and E. W. R. Steacie, *Can. J. Chem.*, **33**, 47 (1955).
8) A. Shepp, *J. Chem. Phys.*, **24**, 939 (1956).
9) R. N. Birrell, R. F. Smith, A. F. Trotman-Dickenson and H. Wilkie, *J. Chem. Soc.*, 1957, 2807.

According to Kerr and Trotman-Dickenson[10], the rate constants of hydrogen abstraction from thiols by methyl radical at 30°C are

MeSH 1.8, EtSH 3.5, Pr^{i}SH 4.1, Bu^{i}SH 5.9

in 10^{-7} mol^{-1} cc. sec^{-1}. From these values they estimated the activation energies between 4.9 and 5.6 kcal. mol^{-1}, assuming $A=10^{11.3}$ mol^{-1} cc. sec^{-1}. If the estimations given by these two studies are accepted altogether and the same value of A is assumed for reaction 5, E_5 can not be lower than 5.6 kcal. mol^{-1}, while a much lower value of 2.6 kcal. mol^{-1} has actually been found in this work. Presumably, there is some error in the order of reactivity estimated by Birrell et al. on the basis of qualitative considerations; although this order of reactivity for a series of thiols from methane thiol to isobutane thiol is in agreement with that of rate constrants found by Kerr and Trotman-Dickenson, and hence may be taken as established, there seems to be no convincing evidence for the least reactivity of hydrogen sulfide[11]. The expression for k_5 obtained in the present work gives $k_5=3.3\times10^9$ mol^{-1} cc. sec^{-1} at 30°C, a value far greater than Kerr and Trotman-Dickenson's rate constants for thiols cited above.

The results given in Table I show that the rate of formation of carbon monoxide, on the whole, increases with temperature in agreement with the previous observation[12-14] on the quantum yield of carbon monoxide. There is some indication in the table at low temperatures that the addition of a small quantity of hydrogen sulfide increases the rate of formation of carbon monoxide, while greater concentration of hydrogen sulfide lowers the rate though the effect is not great at high temperatures. The probable explanation for these findings seems to be given by the promotion of the primary decomposition by hydrogen sulfide and the reaction of acetyl radical with hydrogen sulfide, though anything conclusive cannot yet be drawn at present on these problems.

10) J. A. Kerr and A. F. Trotman-Dickenson, ibid., **1957**, 3322.
11) Birrell et al. themselves described that their interpretation of the results with hydrogen sulfide was somewhat uncertain.
12) R. Spence and W. Wild, *J. Chem. Soc.*, **1937**, 352.
13) D. S. Herr and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **62**, 2052 (1940).
14) H. W. Anderson and G. K.Rollefson, ibid., **63**, 816 (1941).

Summary

Acetone has been photolyzed in the presence of the varied amounts of hydrogen sulfide in the temperature range from 50° to 140°C. From the analysis of the products at low conversions the initial rates of formation of carbon monoxide, methane and ethane have been determined, which, combined with the mechanism of acetone photolysis already established, give the values of $k_5/k_3^{1/2}$, where k_5 and k_3 are respectively the rate constants for the reactions $CH_3+H_2S=CH_4+HS$ and $CH_3+CH_3=C_2H_6$. Accepting $k_3=10^{13.38}$ mol^{-1} cc. sec^{-1} with zero activation energy as recommended by Shepp, the rate constant of the abstraction reaction is represented by $k_5=10^{11.4}\exp(-2.6\text{ kcal. mol}^{-1}/RT)$ mol^{-1} cc. sec^{-1}.

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Temperature Dependence of the Formation of NiO-Li$_2$O Solid Solution

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Since Verwey[1] extensively studied the semiconductivity of a solid solution of lithium oxide in nickel oxide, many investigators[2,3,4] have studied the physical or catalytic properties of the solid solution. In the previous papers[1,2,3,4] the solid solution of NiO-Li$_2$O was formed by heating the mixture of nickel oxide and lithium carbonate. Unfortunately, the dissolved lithium oxide was not determined chemically and was thought to be the same as the added lithium oxide. It is expected that the amount of free lithium oxide is high when the sample is heated at a low temperature and the amount of evaporated lithium oxide is high when the sample is heated at a high temperature in the process of the NiO-Li$_2$O solid solution formation. Accordingly, it is desiarble to determine the amount of the dissolved lithium oxide.

The mixture of nickel oxide and 5 or 10 at. % of lithium was heated and studied in the previous papers[1,4]. In the present experiment about 18 at. % of lithium equivalent to 4.15 wt. % of lithium oxide was mixed. Since the dissolved lithium oxide became constant after a heating period of 3 hr. at 800°C, the mixture of nickel oxide and lithium carbonate which was equivalent to 4.15 wt. % of lithium oxide was heated for 3 hr. at various temperatures. Chemical analysis of lithium oxide was carried out by a flame photometry[5]. Nickel oxide is not soluble in cold dilute acetic acid but lithium carbonate or free lithium oxide is soluble in it. The amount of lithium oxide dissolved in nickel oxide or free oxide was determined by the extraction method and the result is shown in Table I.

Table I shows that the amount of lithium oxide dissolved in nickel oxide is very small when the sample is heated below 600°C and increases with an increase in the heating temperature up to 800°C, but decreases above 1000°C. On the other hand, the amount of free lithium decreases with an increase in the temperature. It is seen that there is a relatively large amount of free lithium oxide present when the sample is heated at high temperatures of 1400 and 1500°C. The amount of lithium oxide evaporated increases remarkably with an increase in the temperature. Table I shows that the mixture heated at 800°C loses one half of the lithium oxide added and the mixtures heated at 1400 and 1500°C have only one tenth of the lithium oxide added. High temperatures are not suitable for the formation

TABLE I. CHEMICAL ANALYSIS AND ELECTRICAL RESISTANCE OF THE MIXTURE HEATED AT VARIOUS TEMPERATURES

Heating temp. (°C)	Free Li$_2$O (wt. %)	Dissolved Li$_2$O (wt. %)	Evaporated Li$_2$O (wt. %)	Electrical resistance (Ω cm.)
unheated	4.15	0	0	3.3×10^{6}
200	4.15	0	0	3.3×10^{6}
300	4.15	0	0	1.2×10^{6}
400	4.15	0	0	4.8×10^{5}
500	4.15	0	0	1.8×10^{4}
600	4.00	0.07	0.08	3.5×10^{2}
800	0.60	1.39	2.16	8.0×10
1000	0.32	1.34	2.49	8.2×10
1100	0.31	1.21	2.63	8.8×10
1200	0.26	0.84	3.05	1.3×10^{2}
1300	0.18	0.78	3.19	1.8×10^{2}
1400	0.11	0.34	3.70	9.2×10^{2}
1500	0.10	0.22	3.83	1.1×10^{2}

1) E. J. Verwey et al., *Philips Res. Rep.*, **5**, 173 (1950).
2) A. Cimino et al., *Z. phys. Chem. N. F.*, **16**, 101 (1958).
3) G. Parravano, *J. Am. Chem. Soc.*, **75**, 1452 (1953).
4) P. Fensham, ibid., **76**, 969 (1954).
5) T. Takeuchi et al., *Rep. Government Ind. Res. Inst. Nagoya (Nagoya Kogyo Gijitsu Shikenjo Hokoku)*, **6**, 719 (1957).

of the solid solution of lithium oxide in nickel oxide, and a temperature range of 800 to 1000°C is suitable.

Since an amount of lithium oxide less than 0.01 wt. % is not found by the flame photometry, the amount of lithium oxide dissolved in nickel oxide below 600°C could not be determined exactly. The electrical resistance of nickel oxide has been known to be sensitive to the foreign atoms incorporated with the lattice[1]. In order to find the temperature at which lithium oxide starts to dissolve in nickel oxide, the electrical resistance of the mixtures heated at various temperatures was measured at room temperature by a method similar to that described by Griffith[6]. The electrical resistance of the mixtures decreases remarkably with an increase in the temperature up to 800°C, and increases with a temperature above 1000°C. It is clearly seen from Table I that the electrical resistance of the mixture heated at 300°C is smaller than that of the pure nickel oxide. As the pure nickel oxide was prepared from ignition of nickel sulfate at 900°C in air for 10 hrs., its electrical resistance is not thought to vary when the oxide is heated below 900°C in air. It is found that NiO-Li_2O solid solution starts to be formed about 300°C.

In order to confirm the fact, electrical resistance of pure nickel oxide and of the mixture were measured at a heating rate of 100°C/hr. from room temperature to 600°C. Fig. 1 clearly shows that the electrical resistance of the mixture becomes lower about 300°C than that of the pure nickel oxide. It is concluded that lithiuum oxide starts to dissolve in nickel oxide at about 300°C.

Bevan and coworkers[7] have suggested that diffusion in ionic compound only becomes appreciable above 0.5 T_m, where T_m is the melting point absolute. Since the melting point of nickel oxide is about 2000°C, the temperature of 300°C is equivalent to 0.25 T_m. It is found that the diffusion of lithium oxide in nickel oxide can clearly be observed by this suitable method even at 0.25 T_m.

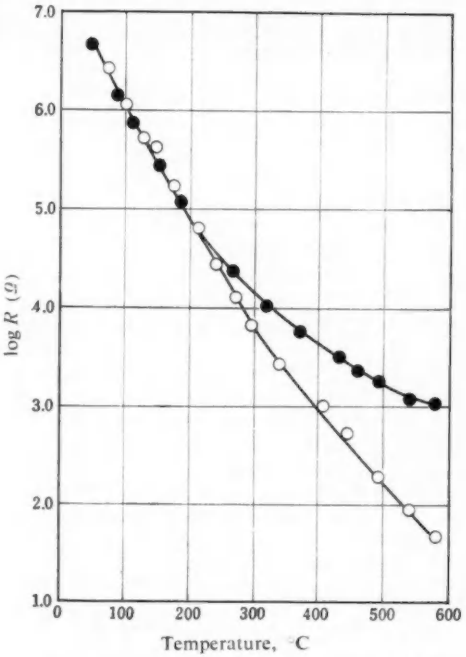

Fig. 1. Electrical resistance of pure nickel oxide (●) and the mixture of nickel oxide and lithium carbonate (○) under heating. A heating rate is 100°C/hr.

6) R. H. Griffith, *Disc. Faraday Soc.*, **8**, 258 (1950).
7) D. J. M. Bevan et al., *J. Chem. Soc.*, **1949** 1729.

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*An Attempted Preparation of Optically Active Organometallic Compounds as Polymerization Catalysts**

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A number of investigations on isotactic polymerization have been carried out in recent years. As regards the mechanism of isotactic polymerization by heterogeneous catalysts, it seems to be of great interest to see if the use of optically active organoaluminum compound in combination with a titanium halide might influence the steric structure of the resulting polymer.

Polymerization of Styrene with an Optically Active Triamylaluminum.—From the viewpoint mentioned above, we attempted to prepare trialkylaluminum containing three optically active 2-methylbutyl groups, starting from (−)-2-methylbutanol of 96% optical purity, $[\alpha]_D^{19°} = -5.70°$.

(−)-2-Methylbutanol was purified by repeated fractional distillation of fusel oil through a Stedman column of about 70 theoretical plates. Calculation of the optical purity is based on the value −5.90° for the pure substance[1]. Treatment of the alcohol with thionyl chloride and pyridine gave (+)-2-methylbutyl chloride of 95% purity, $[\alpha]_D^{14°} = +1.62°$ (+1.70° for the pure substance[2]).

A widely used preparative method of organoaluminum compounds is that using the reaction between metallic aluminum and an alkyl halide. The method, however, was by no means feasible in the case of higher alkyl halides, such as amyl chloride, because of the occurrence of vigorous decomposition reaction[3], and hence an alternative method was adopted in the present work as shown in the following equations:

$$HgCl_2 + 2AmMgCl \rightarrow Hg(Am)_2 + 2MgCl_2 \quad (1)$$

$$2Al + 3Hg(Am)_2 \rightarrow 2Al(Am)_3 + 3Hg \quad (2)$$

$$(Am = -CH_2-CH(CH_3)-CH_2-CH_3)$$

(+)-Bis-(2-methylbutyl)mercury was obtained in 80% yield by the reaction of Eq. 1. An ethereal solution of 2-methylbutylmagnesium chloride (from 11.0 g. of the active chloride) and mercuric chloride (12 g.) was refluxed for one hour, and then after the removal of ether by distillation the residual mass was heated in an oil bath at 120°C for one hour. The reaction mass was combined with the ether distillate, decomposed by saturated aqueous ammonium chloride, and distilled to yield the product, b. p. 135～7°C (30 mmHg), $d_4^{27.5} = 1.657$, $[\alpha]_D^{27.5°} = +7.65°$.

Found: Hg, 56.6%. Calcd. for $C_{10}H_{22}Hg$: Hg, 58.5%.

As the reaction between metallic aluminum and (+)-bis-(2-methylbutyl)mercury was found to be very vigorous, leading occasionally to decomposition of the product, the exothermic reaction was suppressed by the portion-wise addition of granular aluminum into (+)-bis-2-methylbutyl)mercury, which was kept at 100～110°C in an oil bath. The yield of tris-(2-methylbutyl) aluminum was 56% based on (+)-bis-(2-methylbutyl)mercury used, b. p. 85～105°C (0.5 mmHg).

Found: Al, 11.50%. Calcd. for $C_{15}H_{33}Al$: Al, 11.24%.

The optical purity of tris-(2-methylbutyl)-aluminum thus obtained was estimated by the following procedures, i.e., oxidation with oxygen, subsequent hydrolysis to 2-methylbutanol, and checking its optical rotatory power:

$$2Al(Am)_3 + 3O_2 \rightarrow 2Al(OAm)_3 \quad (3)$$

$$Al(OAm)_3 + aq.\,HCl \rightarrow AlCl_3 aq. + AmOH \quad (4)$$

The recovered 2-methylbutanol was found to have an optical purity of 27%, $[\alpha]_D^{30°} = -1.58°$, which indicates that an extensive racemization had taken place in some stages of the synthetic process (Eqs. 1 and 2) or of recovering process (Eqs. 3 and 4). In our experiment, therefore, the optical purity of tris-(2-methylbutyl)aluminum should be estimated at 27% at the lowest.

Polymerization of styrene was carried out at 70°C in *n*-heptane using this aluminum compound (0.3 g.) in combination with titanium trichloride (3 g.) for 2 to 7.5 hr. The isotactic fractions of the polymers showed no difference

*) Paper IV in a series on "Stereoregular Polymers". Presented at the Symposium of High Polymers, Osaka October 14, 1958.

1) W. Markwald and A. Mackenzie, *Ber.*, **34**, 485 (1907).

2) A. Mackenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 698 (1913).

3) A. V. Grosse and J. M. Mavity, *J. Org. Chem.*, **5**, 108 (1940).

4) The content of mercury was determined by decomposition of the sample with sulfuric acid in a Kjeldahl flask and by titration of mercuric ions with ammonium rhodanate, M. Hiral and R. Hayatsu, *J. Pharm. Soc. Japan* (*Yakugakuzashi*), **70**, 76 (1950).

in the physical properties, such as melting points, X-ray diffraction pattern and optical rotation in toluene solution, in comparison with isotactic polystyrenes that were prepared with racemic tris-(2-methylbutyl) aluminum and titanium trichloride.

Polymerization of Styrene with Optically Active Amylsodium. — In the course of our study on the polymerization of styrene with Alfin catalysts, it was found that amylsodium alone could produce isotactic polystyrene in a suitable solvent, though in a small yield, together with a large amount of atactic polymer. Based on this observation, the amylsodium prepared from optically active amyl chloride was tested in the same way. Amylsodium was prepared from (+)-2-methylbutyl chloride and sodium dispersion in the usual manner[5] and was used as a catalyst in *n*-heptane solvent. However, the isotactic polystyrene here obtained showed again no unusual character and was quite identical with that obtained by an inactive catalyst, isoamylsodium.

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5) J. J. R. Williams, J. Van Den Berghe, K. R. Dunham and W. J. Dulmage, *J. Am. Chem. Soc.*, **79**, 1716 (1957).

Alkylalkoxypolysiloxanes. VIII.[1] *Lower Members of Cyclic Methyl- and Ethyl-isopropoxypolysiloxanes*

By Rokuro OKAWARA and Masuo KATAYAMA

(Received November 11, 1959)

Cyclic trisiloxane, the first member of the cyclic polysiloxanes, has been known. While there were found stable compounds such as dialkyl cyclotrisiloxanes and $(C_2H_5Si(OC_2H_5)O)_3$[2], a group of unstable compounds was also known. Spontaneous changes of physical constants were reported with those unstable cyclotrisiloxanes; $((CH_3)HSiO)_3$[3], $((C_2H_5)HSiO)_3$[4], $(CH_3Si(OC_2H_5)O)_3$[2] and $((C_2H_5O)_2SiO)_3$[5].

In this paper, the preparation and properties of cyclic polysiloxanes as indicated by the following formula will be described.

$$(RSi(OC_3H_7\text{-}i)O)_n \quad R=CH_3 \text{ and } C_2H_5;\ n=3 \text{ and } 4$$

One of the objects of this paper is to assure that the rapid hydrolysis method[2,5] developed by the author is applicable for the preparation of cyclotrimers, and the other is to obtain some knowledge of their stability.

The results showed that the cyclic trimer together with the tetramer were formed by using a considerable dropping rate. Comparing the yield of cyclotrimers, the ethyl compound is formed more easily than the methyl compound in those conditions. The infrared absorption spectra of those cyclotrimers showed, as in the case of $(CH_3Si(OC_2H_5)O)_3$[2,6] and $(C_2H_5Si(OC_2H_5)O)_3$[2], a strong absorption at 1023 cm^{-1} which would likely be attributed to the vibration of Si-O bond in cyclotrisiloxane ring. Though a measurable strain[7] would be expected in the cyclotrisiloxane ring of those compounds, no increase of the refractive index,

TABLE I. RESULTS OF THE HYDROLYSIS

Dichlorosilane (1 mol.) was added to the ice-cooled hydrolyzing mixture which consisted of pyridine (2 mols.), water (1 mol.) and 250 g. of benzene.

Expt.	Dichlorosilane	Droppping rate g./min.	Hydrolyzate: Total yield (%)	Composition (%) C_3**	C_4**	Residue
1	I*	15	57	13	16***	71
2	I	30	65	13	20	67
3	II*	20	75	32	10	58

* I: $CH_3(i\text{-}C_3H_7O)SiCl_2$,
II: $C_2H_5(i\text{-}C_3H_7O)SiCl_2$

** C_3: Cyclic trimer
C_4: Cyclic tetramer

*** Gelation occurred in still-pot after 16% of C_4 has distilled out.

1) Part VII of this series, R. Okawara and S. Imaeda, This Bulletin, **13**, 194 (1958).
2) R. Okawara, G. Minami and Z. Oku, ibid., **31**, 22 (1958).
3) S. D. Brewer, *J. Am. Chem. Soc.*, **70**, 3962 (1948).
4) R. Okawara, U. Takahashi and M. Sakiyma, This Bulletin, **30**, 608 (1957).
5) R. Okawara, S. Hotta and T. Shimura, ibid., **28**, 541 (1955).
6) R. Okawara, ibid., **31**, 154 (1958).
7) T. Tanaka, ibid., **34**, 282 (1960).

Table II. Cyclic polysiloxanes

Polymer size n	Boiling point °C/mmHg	Refractive index n_D^{20}	Density d_D^{20}	Molar refraction found (calcd.)*	Molecular weight found (calcd.)**	Anal. Si, % found*** (calcd.)
	$(C_2H_5Si(OC_3H_7\text{-}i)O)_n$					
3	67/1	1.3973	0.9912	86.23	348	23.80
				(85.98)	(354.6)	(23.76)
4	97/1	1.4023	1.0009	115.09	—	23.77
				(114.64)	(472.8)	(23.76)
	$(C_2H_5Si(OC_3H_7\text{-}i)O)_n$					
3	92/1	1.4129	0.9817	100.74	407	21.22
				(99.87)	(396.7)	(21.24)
4	125/1	1.4177	—	—	—	21.22
						(21.24)

* Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).
** Cryoscopic measurement in benzene.
*** Silicon was determined by decomposing the sample with concentrated suluric acid.

due to a spontaneous decomposition, was observed with the samples sealed in a soft glass ampule within one year.

Experimental

Starting Materials. — Methyltrichlorosilane used in these experiments was supplied from the Shinetsu Chem. Ind. Co. Ethyltrichlorosilane was obtained from the product of silicon-ethylchloride reaction. Methylisopropoxydichlorosilane (I) and ethylisopropoxydichlorosilane (II) were prepared by adding 1 mol. of isopropanol to 1 mol. of those trichlorosilanes, respectively. After the addition, the mixture was aerated with stirring to drive off the hydrogen chloride at room temperature. Then the mixture was fractionated through a Stedman column of about 20 theoretical plates. Redistilled dichlorosilanes were taken for the starting materials.

Methylisopropoxydichlorosilane (I) b. p. 112.5°~113°C (Reported[8]: b. p. 110°~111°C)

Found: Cl, 41.1. Calcd. for (I): Cl, 41.0%.

Ethylisopropoxydichlorosilane (II) b. p. 137°~8°C (Reported[9]: b. p. 67°C/60 mmHg)

Found: Cl, 37.5. Calcd. for (II): Cl, 37.9%.

Hydrolysis and Fractionation of the Hydrolyzate.—Hydrolysis was carried out as described in the preceding papers.[2,5] The results are summarized in Table I.

The composition of the hydrolyzate was determined by fractionation through a Stedman column of about 50 theoretical plates. In Expt. 1, gelation occurred in a still-pot after 16% of C_4 distilled out; accordingly the fractionation of the other runs were carried out with the distillable fraction which was obtained from the hydrolyzate through a simple distillation. Comparing the yield of C_3, the ethyl compound is more easy to be formed than the methyl compound.

The fractions which exhibited constant boiling points and refractive indicies were taken for the samples and their physical constants are given in Table II.

Infrared Spectra and Stability. — Infrared absorption spectra were obtained with a Hilger H-800 infrared spectrophotometer with a rock salt prism. In the range 700~1300 cm^{-1}, samples were observed as solution in carbon disulfide. The positions of the strong bands which appeared in the range 1000~1100 cm^{-1} are shown in Table III.

Table III

Compound	Absorption Spectra (in cm^{-1})		
$(CH_3Si(OC_3H_7\text{-}i)O)_3$	1023	1044	—
(〃)$_4$	—	1044	1086
$(C_2H_5Si(OC_3H_7\text{-}i)O)_3$	1024	1045	—
(〃)$_4$	—	1043	1087

All the samples shown in Table II, which were sealed in a glass ampule, gave no changes of refractive index within one year.

Summary

1) Methyl- and ethyl-isopropoxydichlorosilane were hydrolyzed with considerable dropping rate using pyridine as an acid acceptor.

2) Methyl- and ethyl-isopropoxycyclotrisiloxane have been prepared and characterized. Those compounds were found to be stable.

3) Methyl- and ethyl-isopropoxycyclotetrasiloxane have been prepared and characterized.

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Absorption Spectra of Dyes. V[1]*. The Composition and Intermolecular Charge Transfer Spectra of Complexes Formed in Aqueous Solution of the Mixture of Chlorazol Sky Blue FF and Chrysophenine G*

By Teruaki KOBAYASHI, Yoshié TANIZAKI and Noboru ANDO

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Most of the binary mixtures of dyes in aqueous solution studied before showed more or less non-additive spectra[1-6]. Of these dyes the pair of Chlorazol Sky Blue FF and Chrysophenine G revealed the most remarkable change in spectrum. This pair was first studied by Neale and Stringfellow[2], and then in more detail by Derbyshire and Peters[4]. According to the latter workers, only a 1:1 complex is formed between Chrysophenine G and Chlorazol Sky Blue FF in equimolar solution or in the presence of an excess of Chlorazol Sky Blue FF at room temperature, while higher complexes are formed to a certain extent in the presence of an excess of Chrysophenine G. However, they made no mention of the composition of these higher complexes. In the hope of obtaining some information about the composition of the higher complexes and then interpreting the spectral change observed on the basis of quantum chemical concept, this combination has been studied in greater detail.

A series of studies of binary mixtures of Chlorazol Sky Blue FF with some other dyes have shown that the relatively small spectral change observed in mixtures of some monoazo and disazo dyes may be explained by the perturbation between molecular orbitals of two component dyes caused by the formation of loose complexes[1,5]. However, it has been impossible to apply this concept to more compact complexes: a large spectral change which appeared in a binary mixture of Chlorazol Sky Blue FF has been unable to be explained without the concept of intermolecular charge transfer[1]. As the authors pointed out before, the mixture of Chlorazol Sky Blue FF and Chrysophenine G also shows a spectral change which implies the occurrence of charge transfer[1]. Therefore, this pair, which is considered to be a typical example of these sorts of dyes having the intermolecular charge transfer phenomenon, seems to be most suitable for our purpose.

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Experimental

Preparation of Samples.—The purification of the dyes and the preparation of dye solutions followed the same methods as explained in the previous paper[1].

Absorption Spectra.—All the absorption spectra of dye solutions were measured by a Shimadzu QR-50 spectrophtometer at room temperature (27 ~ 30°C). Cells used were 0.2, 0.5 and 1 cm. thick.

Hereafter Chlorazol Sky Blue FF and Chrysophenine G will shortly be called Blue (or B) and Yellow (or G), respectively.

Results and Discussion

1. The Composition of Complexes Formed in Solutions.—As is shown in Fig. 1, absorption spectra of mixtures of Blue and Yellow at

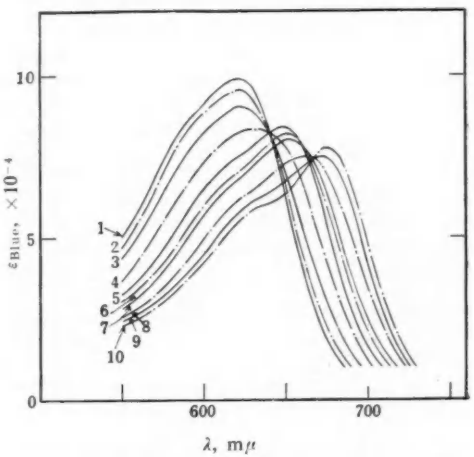


Fig. 1. Absorption spectra of mixtures of Blue and Yellow in aqueous solution at room temperature (ca. 27°C). The concentration of Blue is 1.00×10^{-5} mol./l. The ratio of the concentration of Yellow to that of Blue is 1-0, 2-0.105, 3-0.313, 4-0.610, 5-1.03, 6-1.55, 7-2.07, 8-4.18, 9-8.27 and 10-51.5.

wavelengths corresponding to the first absorption band of Blue (620 mμ) show a characteristic change, with an increase in the concentration of Yellow added into the solution containing a constant amount of Blue (1.00×10^{-5} mol./l.). It is already known[4] that, while the concentration of Yellow does not exceed that of Blue, spectra of mixtures of this pair have an isosbestic point at about 640 mμ accompanied with a new clear absorption band at 650 mμ. Fig. 1 clearly shows that, when the concentration of Yellow has increased more than four times as high as that of Blue, the second isosbestic point appears at about 670 mμ and 650 mμ band disappears, followed by the appearance of a new band at 675 mμ. Since Yellow does not absorb light in the wavelength region shown in the figure, these two isosbestic points mean that each molecule responsible for the 650 mμ band contains in itself one Blue molecule (the first isosbestic point), and that each molecule responsible for the 675 mμ band contains in itself one molecule of the complex (the second isosbestic point).

As has already been known, the 650 mμ band is due to a 1 : 1 complex[4]. Then, the molecular species of the 675 mμ band may be considered to be a complex made up of a 1 : 1 complex and Yellow in the ratio 1 : 1. Now, let us suppose that the molecular species which shows the 675 mμ band is a 1 : 2 complex richer in Yellow and that the following equilibriums exist in solutions.

$$B + G \rightleftarrows BG \qquad (K_1)$$

$$BG + G \rightleftarrows BG_2 \qquad (K_2)$$

It is possible to calculate the equilibrium constants (K_1 and K_2) corresponding to the above equilibriums, from observed obtical densities in accordance with the mass action law. They were calculated here by use of the difference ΔD between the sum of observed optical densities of the component dyes and the optical density of the corresponding mixture at 620 mμ, according to the usual method[3,6]. Since the observed optical density of the mixture is, in practice, the sum of those of the single dyes and the complexes, the calculation is complicated. Therefore, an approximate one was performed. As the figure shows clearly, the amount of 1 : 2 complex is negligibly small in the concentration region [B] > [G] (where [B] and [G] mean the initial concentrations of Blue and Yellow. respectively). Consequently, the value of K_1 was calculated from observed optical densities in the region [B] > [G]. The optical density at 620 mμ decreases with an increrase of [G], approaching to a certain value as [G] becomes large relative to [B]. This value may be considered to be due only to the 1 : 2 complex, BG_2. Thus the molecular extinction coefficient of BG_2 may be known, and by use of it, $K(=K_1K_2)$, the overall equilibrium constant of the formation of the complexes, may be calculated. K_2 can easily be obtained from K and K_1. Calculated values of K_1 and K_2 were about 6×10^5 and 5×10^4, respectively, at 27°C.

Now as the values of K_1 and K_2 were thus decided, the concentrations of BG and BG_2 corresponding to any amounts of Blue and Yellow will be obtained, according to mass action equations, hence the difference of optical densities ΔD will be calculated by use of them. Calculated $\Delta D\sim$[G] curves when the initial concentration of Yellow is varied with that of Blue kept constant are shown by full lines in Fig. 2,

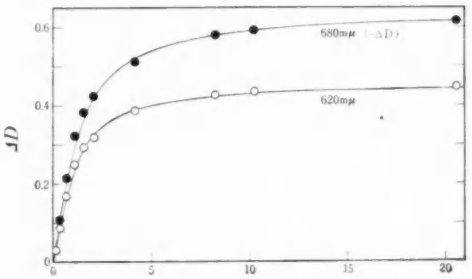


Fig. 2. The difference in optical densities when the concentration of Blue is constant (1.00×10^{-5} mol./l.) at 27°±1°C. 1 cm. thick.
Full lines: calculated differences
Black and white circles: observed differences corresponding to the respective curves

in which the lower and upper curves show the differencce at 620 mμ and at 680 mμ, respectively. The latter is described as $-\Delta D$ because it has negative values. Observed values corresponding to each curve are shown by white and black circles. They are coincident well with the respective calculated curves.

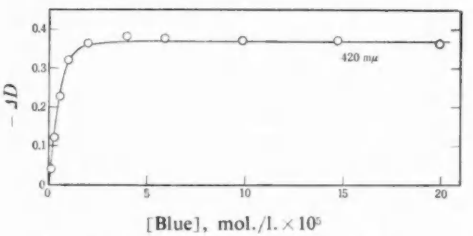


Fig. 3. The difference in optical densities when the concentration of Yellow is constant (1.00×10^{-5} mol./l.) at 28°±1°C. 1 cm. thick.
Full line: calculated difference
White circles: observed differences corresponding to the calculated curve

A corresponding calculation was then made at 420 mμ, the concentration of Yellow being kept constant. The result ($-\Delta D \sim$ [B] curve) is shown by a full line in Fig. 3, in which the white circles are corresponding observed values. The coincidence between the observed and the calculated values is also satisfactory in this case.

As seen above, each of the $\Delta D \sim$ [G] and the $\sim$ [B] curves calculated by use of K_1 and K_2, of which values were obtained from the observed optical densities at 620 mμ, explains the observed values well. This satisfactory coincidence between the observed and the calculated values of ΔD means the propriety of the assumption that a 1 : 1 complex and a 1 : 2 complex are formed in equilibrium in the mixture solution. Further it affirms that the obtained values of K_1 and K_2 are proper.

Now, it has become clear that two sorts of complexes exist in the mixture solution, in addition to the component dyes. Therefore, the behavior of the spectral change shown in Fig. 1, i. e., the shift of the first absorption band from 620 mμ to 650 mμ and to 675 mμ through the two isosbestic points with an increase in concentration of yellow, may be expressed in the quantitative relation among these components and complexes. The consentrations of Blue and the two complexes change with an increase in amount of Yellow as shown in Fig. 4, in which Curves I, II and III show the concentrations of free Blue, BG and BG_2, respectively. As the figure shows, the existence of BG_2 is negligible when it is compared with the others, in the region where the amount of Yellow is less than 0.5×10^{-5} mol./l. Consequently the spectral change of the mixture will be governed only by the amounts of free Blue and BG (the first isosbestic point). When the concentration of Yellow is further increased, free Blue decreases to a nigligible amount, hence the spectral change is governed only by the amounts of BG and BG_2 (the second isosbestic point). Thus the change in spectra of the mixtures shown in Fig. 1 will well be understood through the relation between the concentrations of the components and the complexes shown in Fig. 4.

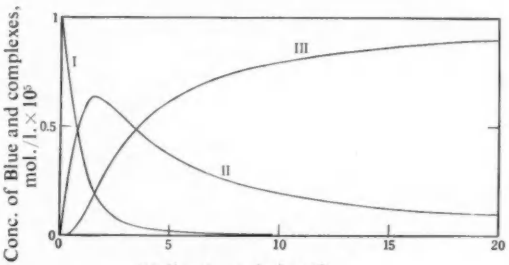


Fig. 4. The changes in concentrations of Blue and the complexes with that of Yellow when the initial concentration of Blue is 1.00×10^{-5} mol./l.
I: free Blue, II: BG, III: BG_2

2. The Change in Absorption Spectra.—The discussion in the previous section has clarified that a 1 : 1 complex BG and a 1 : 2 complex BG_2 are formed in aqueous solution of the mixture of Blue and Yellow. The equilibrium constants (K_1 and K_2) for these complexes have also been obtained. Therefore, absorption curves of the complexes can be drawn from observed absorption spectra of mixtures. The curves shown in Fig. 5 are the absorption spectra of BG and BG_2 thus obtained*. Inspection of the absorption spectra of the components and the complexes

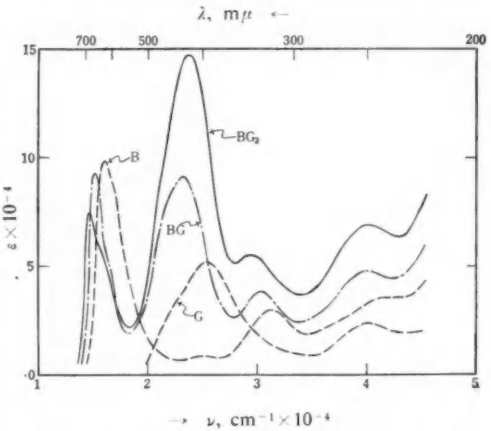


Fig. 5. Absorption spectra of the complexes and the component dyes

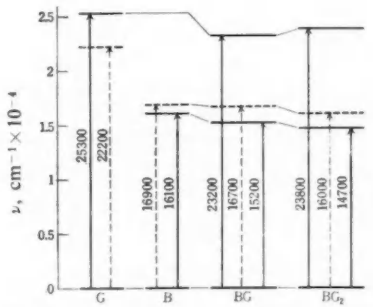


Fig. 6. Observed transition energies (cm^{-1}) of Yellow (G), Blue (B) and the complexes (BG and BG_2)

* Since these curves were made from absorption specra which were converted from those measured in various cells different in thickness so as to correspond to the unit cell, their molecular extinction coefficients and maximum wavelengths shown in the figure may have some errors.

shows that the first absorption bands shift to longer wavelengths with a change from Blue to BG_2; on the other hand, the absorption of BG corresponding to the first absorption band of Yellow (395 mμ) is markedly shifted to longer wavelengths (430 mμ) with a remarkable increase in intensity, while that of BG_2 to shorter wavelengths (420 mμ) than that of BG is. To show these changes more clearly, the transition energies (cm^{-1}) of Blue, Yellow, BG and BG_2 are given in Fig. 6, where the dotted lines mean absorptions corresponding to shoulders. The absorptions illustrated in Fig. 6 seem to show a regular change, except those in the shorter wavelength region, in view of the fact that they shift to longer wavelengths with a change from Blue to BG_2. The absorptions of the complexes in the shorter wavelength rigion seem to have an unusual behavior. Perhaps they are charge transfer spectra, as the following discussion will suggest.

The first absorption bands of dyes are generally considered to be due to conjugated double bond chains connected with auxochromes. According to the VB theory, the first absorption bands of Blue and Yellow may be considered to be owing to resonances between the following extreme structures.

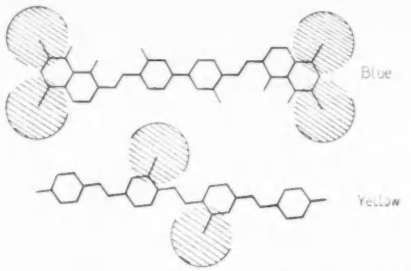
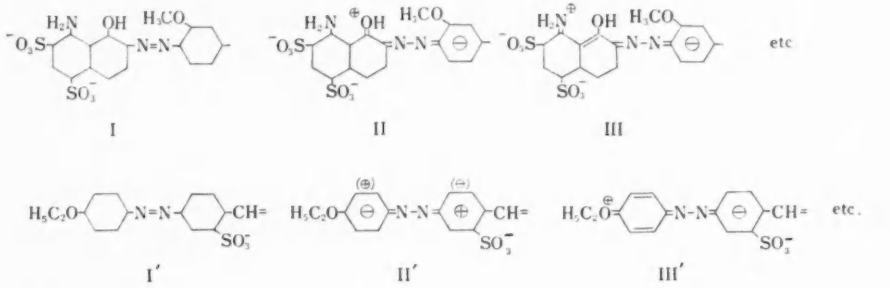


Fig. 7. Models of Blue and Yellow. The shadowed circles mean sulfonic groups.

pointed out before[1] and the structures in Fig. 7 show clearly, Blue and Yellow might approach close each other without accepting the repulsion of their charged groups, if they form complexes with their molecular axes in parallel with each other. In such structures, the auxochromes of Blue may have higher possibility of being covered by the conjugated system of their partners than those of Yellow, so unshared π-electrons of the auxochromes of Blue may be more affected than those of Yellow. These conditions may make the ground state of Blue unstable, the contribution of structure I to it



where the half of the structure of each dye is shown. Though there are a number of extreme structures, they are lumped together under the structures of which inner π-electron systems have negative charge. The first absorption band of each dye may approximately be expressed by a transition from the ground state (mainly I or I′) to an excited state (mainly II or II′)**. As

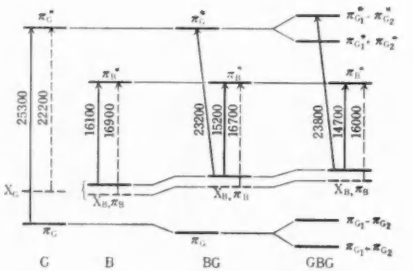
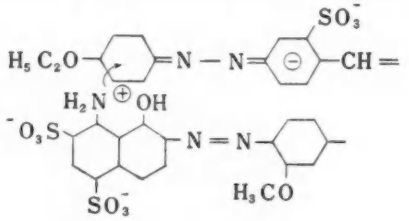


Fig. 8. Schematic representation of electronic transitions among molecular orbitals of Yellow (G), Blue (B) and the complexes (BG and GBG)

** According to empirical facts, auxochromes, which are attached to a naphthalene ring as a coupling component, show, in general, greater effects on absorption spectra, when attached to the inner ring having an azo group. Hence, the excited state of Blue seems to consist mainly of structure II. In case of Yellow, as the effect of OC_2H_5 as auxochrome seems to be weak because of its weak electron donating power relative to NH_2, ect.,[7] it may approximately be considered that the shoulder of the first absorption hand is due to the resonance I′↔III′ and the peak to I′↔II′.

7) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Orgnic Chemistry", Edward Arnold, London, (1957), p. 129.

smaller, and, at the same time, charge transfer from Blue to Yellow easy. The important structure of an excited state in this case may be



in which a mobile electron of Blue in structure II or III transfers to the inner π-electron system of Yellow***.

The same discussion will be given on BG_2. The structure of BG_2 may be considered to be a sandwich type with B in its inside. The two G molecules in this complex are supposed to be close to each other in spite of holding B between them, so it is necessary to take into account an interaction between them: the mixing may occur to some extent between the excited states of G molecules, causing them to split in two different levels. The experimental results suggest that the charge transfer from B may occur to the higher level, though it can not possibly be ascertained.

According to the MO method, the spectral change will be explained as follows. A rough approximation shows that the first absorption bands of the dyes are due to electron transitions of unshared π-electrons of the auxochromes to the lowest vacant orbitals of the inner π-electron systems, i. e., the $X \rightarrow \pi^*$ transitions in Fig. 8****. In case of Yellow (G), this is $X_G \rightarrow \pi_G^*$. As the electron donating power of OC_2H_5 is weak relative to that of NH_2[7], however, this absorption may also be weak. Probably the principal absorption band of G is due to $\pi_G \rightarrow \pi_G^*$. In case of Blue, it is difficult to know which auxochrome X_B corresponds to, because Blue has many auxochromes. Consequently, they are lumped together under X_B.

If Bule and Yellow from the complex BG with the structure mentioned above, the first probable change will arise between π_G and X_B (and π_B), because the auxochromes of B may be affected strongly by the inner π-electron system of G; a repulsion between these MO's will occur to make such a pattern as BG in Fig. 8. It was supposed here that no interaction happens between π_B^* and π_G^*. If a geometrical arrangement of the orbitals X_B and π_G^* in the complex is taken into consideration, the $X_B \rightarrow \pi_G^*$ transition, i. e., an intermoleculer charge transfer, may be expected to occur easily.

Concerning the complex BG_2, as already mentioned, its structure may be as GBG, with the linear molecules standing side by side. Since the G molecules stand close to each other in spite of B existing between them and parallel with each other, the complex has at least one symmetry. Consequently, the two π_G^* orbitals mix to separate into $\pi^*_{G_1} + \pi^*_{G_2}$ and $\pi^*_{G_1} - \pi^*_{G_2}$. As seen in the discussion based on the VB theory, it is also difficult to ascertain to which molecular orbital the charge transfer from B occurs. The experimental results, however, mean that it may be $X_B \rightarrow (\pi^*_{G_1} - \pi^*_{G_2})$. On the other hand, it is clear from the above discussion that the X_B level in GBG is pushed up higher than the one in BG.

Though there is no ground for justifying the relative positions of the molecular orbitals in Fig. 8, the spectral changes shown in Fig. 6 could be explained at least qualitatively by the above discussion based on the MO method. Some parts of the above two discussions were not always perfect, but it should be noted that the spectra of the complexes could not be explained without the concept of charge transfer. Explanation of these specteal changes by a solvent effect caused by the close approach of dye molecules was attempted, without considering the charge transfer, only to fail; the first absorption band of Yellow was insensitive to the change in pH or in solvent. So, it follows that the strong absorptions at about 420 mμ of the complexes can not be explained by a mere solvent effect.

Thus the absorption spectra of the complexes formed of Blue and Yellow could be explained qualitatively on the basis of those of the components. A binary mixture of Blue, in which the formation of a 1 : 1 complex is proved, also showed a change in spectrum which might not be explained without the concept of charge transfer.[1],***** It cannot always be said, however, that its charge transfer occurs in the same mechanism as is considered in the present work. The main reason will be found in the fact that the partner of Blue has no such symmetry in its structure as Yellow has and that the obvious factors suggesting the arrangement of the component dyes in the complex are not found.

*** Since the amino groups have less effect on the spectrum of Blue than the hydroxyl groups and the electron donating power of the former is stronger than that of the latter, as mentioned in footnote 2, an electron of one of the amino groups may be considered to have high possibility of acting in the intermolecular charge transfer. However, it is impossible and unnecessary to confirm the fact.

**** X and π mean the orbital of unshared electrons and the inner π-orbital, respectively.

***** Blue and Durazol Red 2B forms a 1 : 1 complex in aqueous solution (see Ref. 3), of which spectrum seems not to be understood without considering charge transfer.

Summary

1. The change in absorption spectra of mixtures of Chlorazol Sky Blue FF and Chrysophenine G in aqueous solution was stoichiometrically studied in detail and a 1 : 1 complex and a 1 : 2 complex were proved to be formed.
2. The absorption spectra of the complexes were drawn from experimental results by use of the calculated equilibrium constants, and the phenomena of these absorptions were qualitatively explained according to VB and MO methods, with the conclusion that charge transfer spectra from Chlorazol Sky Blue FF to Chrysophenine G appear in the complexes.

The authors wish to express their thanks to Professor Ikuzo Tanaka for his helpful discussion.

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Sodium Iodide-Acetone and Zinc Bromide-Acetone Molecular Complexes

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The molecular compound between sodium iodide and acetone, known as NaI·3 acetone, can be used for the purification of acetone. The nature of the bonding, however, has not been made clear. From conductivity measurements, Rosenthal[1] suggested that the molecular compound was dissociated into Na^+ and $(I \cdot 3 \text{ acetone})^-$ in acetone. This may indicate that the compound has an ionic structure as represented by Na^+ $(I \cdot 3 \text{ acetone})^-$. By infrared studies, Slovokhotova[2] reported that acetone molecules had the enol form when sodium iodide was added, but her explanation does not seem to be plausible.

On the other hand, the complex formed by the addition of iodine or lithium perchlorate to acetone is known as the charge transfer complex stabilized by the electron donor-acceptor interaction[3,4]. The sodium compounds of salicylaldehyde and methylsalicylate[5] are also known to be formed by the same interaction between the Na^+ ion and the C–O and C=O groups, respectively. As for the NaI-acetone complex, the charge transfer force may interpret the intermolecular bonding.

The present study has been undertaken to clarify what sort of force gives rise mainly to the intermolecular bonding of the NaI-acetone and $ZnBr_2$-acetone systems.

1) W. Rosenthal, *Compt. rend.*, **237**, 1537 (1953).
2) N. A. Slovokhotova, *Zhur. Fiz. Kim.*, **25**, 768 (1951), *Chem. Abstr.*, **46**, 2396h (1952).
3) H. Yamada and K. Kozima, *J. Am. Chem. Soc.*, **82**, 1543 (1960).
4) A. D. E. Pullin and J. McC. Pollock, *Trans. Faraday Soc.*, **54**, 11 (1958).
5) H. Yamada, This Bulletin, **32**, 1051 (1959).

Experimental

Guaranteed commercial anhydrous sodium iodide and zinc bromide were used without further purification. Sodium perchlorate was obtained by heating $NaClO_4 \cdot H_2O$ in an air bath. The anhydrous salts were stored in the dark in a desiccator. Acetone was used after drying over anhydrous sodium sulfate and fractionating. The salts were dissolved into acetone and the thin layers of the solutions were obtained by sandwiching them between polyethylene films. The solid sample was made by cooling with the dry ice-ethanol mixture. The infrared spectra were taken with a Perkin-Elmer Model 112 infrared spectrophotometer in the region $400\,cm^{-1} \sim 4000 cm^{-1}$, using KBr, NaCl, CaF_2 and LiF prisms.

The composition of the complex was determined as follows. The salt was dissolved into acetone at room temperature and its concentration was determined by weighing. When the solution was cooled and the complex was crystallized, an excess of acetone was eliminated by suction and the complex was weighed.

Results and Discussion

The wave numbers of the spectra of the NaI- and $ZnBr_2$-acetone systems are shown in Table I and the curves in Figs. 1—5.

The skeletal vibrations of acetone were influenced noticeably by the addition of the salts, while the other bands were not so affected. Concerning the bands splitting into the two components, one of the components can be attributed to the complex and the other to original acetone. Although the separation of the C=O stretching band in NaI-acetone system

TABLE I. WAVE NUMBERS OF SPECTRA FOR ACETONE, NaI-ACETONE AND $ZnBr_2$-ACETONE

Acetone (liquid)	NaI-acetone (liquid)	NaI-acetone (solid)	$ZnBr_2$-acetone (liquid)	Assignment*
1717	1709	1708	1697(s)	A_1 C=O stretching
785	789	790	789	A_1 C-C sym. stretching
1215	1233(s)	1236(s)	1236(s)	B_1 C-C antisym. stretching
530	539(s)	540(s)	540(s)	B_1 C-C=O bending
3411	3405	3401	3401	A_1 C=O stretching overtone
1092	1093	1094	1091	
903	906	910	909	

(s) indicates the band having two components and the wave number is the value for the complex component.

* T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **74**, 915 (1953).

could not be observed, the observed band with the shifted maximum is interpreted as the complexed band closely overlapped with the non-complexed one. The fact that the band shifts observed on complex formation are small suggests that the acetone molecules in the complex are slightly perturbed. The directions and amounts of the shifts are similar to those observed for the iodine-acetone[3] and lithium perchlorate-acetone complexes[4]. These shifts may be interpreted as being due to the changes of the force constants of C=O stretching and C-C=O bending vibrations caused by the formation of the complex, similarly as the case of the iodine-acetone or lithium perchlorate-acetone complex[5].

Since the spectrum of the NaI-acetone complex exhibited a similarity to that of the $NaClO_4$-acetone complex except the absorption caused by the ClO_4^- ion, the formation of the salt-acetone complex may be due to the bonding between acetone and the Na^+ or Zn^{2+} ion.

When the NaI-acetone solution was cooled, the needle crystal was obtained. Its composition was 1 : 5 mole ratio. The spectrum of this crystal contained the original acetone bands and was similar to that of the solution. The C-C antisymmetric stretching band is shown in Fig. 2(b). This curve can be divided into the two Lorentz curves with the maxima at 1236 cm^{-1} and at 1215 cm^{-1}. Intensities were calculated from Ramsay's method[7]. It has been shown[3] that, for the iodine-acetone system, this band does not change in intensity on complex formation. The same may be true for this complex. From this property of the band and the fact that the area intensity ratio between the two bands is about 3 : 2, it follows that three acetone molecules are regarded as those of complexed acetone and the other two as those of non-complexed acetone. Probably the Na^+ ion forms the tetra-coordinate compound having I^- and three acetone molecules as ligands and the other two acetone molecules will be contained in the crystal without coordinating.

The overtone band of the C=O stretching vibration showed a remarkable change. As shown in Fig. 5, this band became broad and was enhanced very much. By subtracting the two bands at 3520 cm^{-1} and at 3620 cm^{-1} from the observed curve for the NaI-acetone system, the dotted curve was obtained. This may be attributed to the overtone band of C=O stretching vibration and not the OH band, because the similar phenomenon was observed for the overtone band of the C=O stretching vibration of the iodine-acetone complex.

Relatively large shifts were observed for the skeletal vibrations belonging to the B_1 type. This differs from the phenomenon observed for the iodine-acetone complex and is probably due to the fact that the mole ratio of the NaI-acetone complex is 1 : 3 even in solution, while that of the iodine-acetone is 1 : 1.

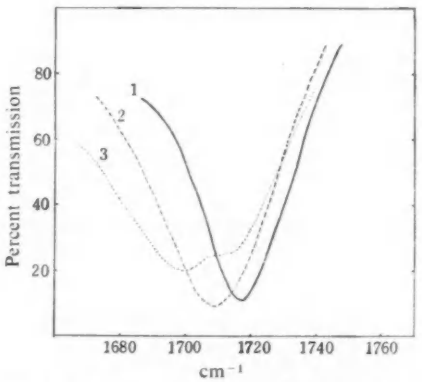
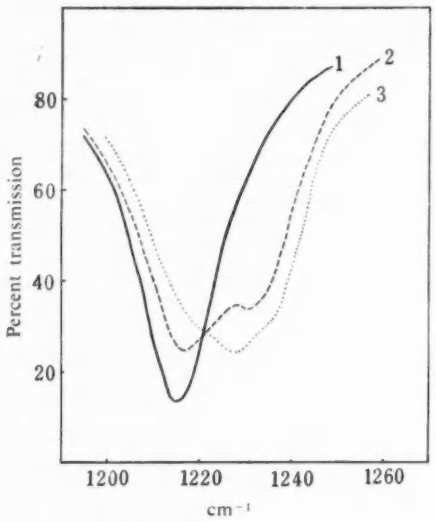
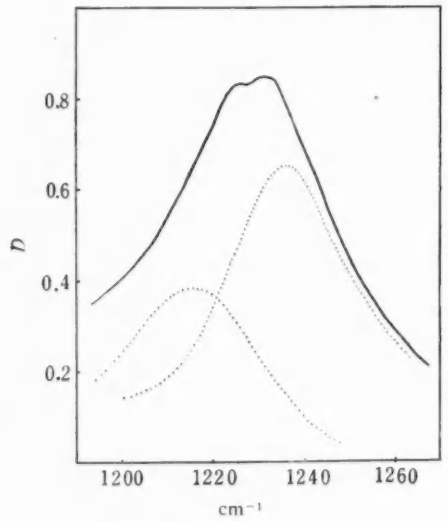


Fig. 1. C=O stretching bands for NaI- and $ZnBr_2$-acetone systems.
1. Pure acetone
2. NaI-acetone solution (saturated)
3. $ZnBr_2$-acetone solution (saturated)

6) K. Kozima and H. Yamada, unpublished.
7) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1956).



(a) Liquid state
1. Pure acetone
2. NaI-acetone in 1 : 10 mole ratio
3. NaI-acetone in 1 : 6 mole ratio



(b) Solid state
Unbroken curve is observed for NaI-acetone solid in 1 : 5 mole ratio. Dotted curves are Lorentz curves.

Fig. 2. C–C antisym. stretching bands of NaI-acetone system.

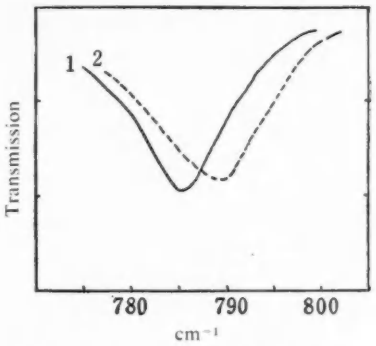


Fig. 3. C–C sym. stretching bands.
1. Pure acetone
2. NaI-acetone solution (saturated)

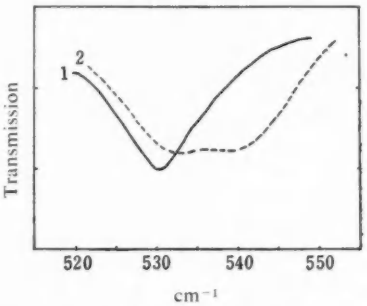


Fig. 4. C–C=O bending bands.
1. Pure acetone
2. NaI-acetone solution (saturated)

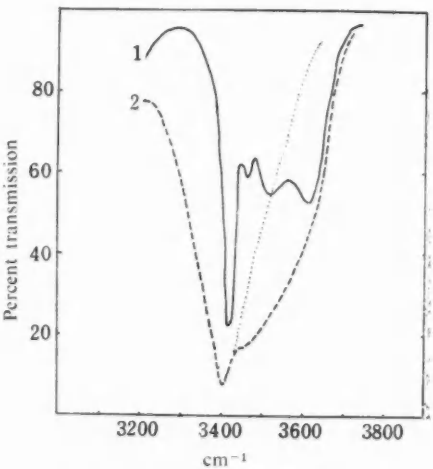
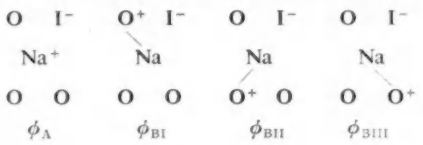


Fig. 5. Overtone bands of C=O stretching vibration.
1. Pure acetone (0.1 mm. cell)
2. NaI-acetone solution (0.1 mm. cell)

From the fact that the frequencies of the acetone band maxima do not vary continuously with salt concentration but the bands show the contour of two components and from the fact that observed shifts are similar to those for the iodine-acetone charge transfer complex, it may be concluded that the formation of the complex is due to the coordination of the lone pair electrons of oxygen atom to the Na^+ or Zn^{2+} ion. No evidence for the enolization of acetone was found. As for the intermolecular bonding of these complexes, the charge transfer force, besides ion-dipole interaction etc., should be taken into account. The wave function of the normal state for the complex may be written by

$$\Psi_N = a\phi_A + b(\phi_{BI} + \phi_{BII} + \phi_{BIII}).$$

Here ϕ_A expresses the no-bond structure and ϕ_{BI}, ϕ_{BII} and ϕ_{BIII} following dative structures.



The author wishes to express her sincere thanks to Professor K. Kozima for his kind guidance during this work.

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*Synthesis of 1,4,7-Cyclononatrione**

By Sin'iti KAWAI, Sanae TANAKA, Kenji TERAI, Masami TEZUKA and Tarozaemon NISHIWAKI

(Received May 26, 1959)

The hydrocarbon $C_{20}H_{20}$ (III) with the complete skeleton of a regular pentagonal dodecahedron has not yet been known. Since the hydrocarbon, which shall be tentatively called "dodecahedrane", will be a very stable, strainless compound, an attemp of its synthesis has been started with the present work.

For the synthesis of dodecahedrane it is necessary to obtain the hypothetical *d, l*-tricyclic compound, I+I′, which shall be temporarily called " tricyclone ". Although there are four asymmetric carbon atoms in the molecule of tricyclone, only one pair of optical isomers, I and I′, are possible and synthesis will lead to a racemate. The tricyclone, having three pairs each of carbonyl and active methylene groups, must be a very reactive compound. Condensation will begin with the collision of two molecules of triyclone in the following combination:

(1) I+I′; (2) I+I and (3) I′+I′.

Case 1 may be divided into three divisions, a, b and c.

(a) Addition starts with cyclobutane ring formation, for instance, with addition of 2′ to 1 and of 2 to 1′.

(b) Addition starts with cyclohexane ring formation, for instance, with addition of 2 to 1′ and of 6′ to 3.

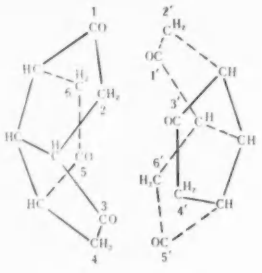
(c) Addition starsts with cyclopentane ring formation, for instance, with addtion of 2 to 3′ and of 4′ to 3.

Both divisions a and b will lead to undefinable polymerization products, while division c may proceed to a dodecahedrane derivative under consecutive additions of 2′ to 1, of 6 to 1′, of 6′ to 5 and of 4 to 5′.

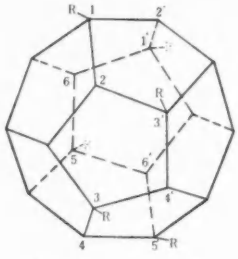
In the presence of an appropriate agent (for instance sodium ethoxide, etc.), I and I′ will be able to add to each other to give a hexahydroxydodecahedrane (II, R=OH) through the narrow reaction route, cace 1, division c, the yield being consequently expected to be small. As soon as the hexahydroxydodecahedrane is formed, it may probably suffer spontaneous dehydration, thus affording dodecahedrahexaene (IV). It is to be noted, that formula IV denotes only a limiting structure, because the conjugated hexaene ring V contained in formula IV will resonate with another limiting structure VA and that the double linkings in the molecule will not be restricted within the one hexaene ring, V↔VA, but will be distributed equally all over the whole system of the twenty carbon atoms. Consequently the dodecahedrahexaene is expected to be a rather stable compound, but its catalytic hydrogenation may afford the desired dodecahedrane (III).

On the other hand, one possibility from case

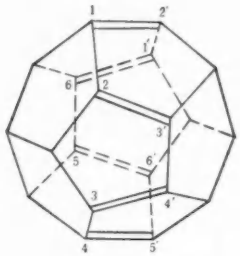
* Read before the Ninth Annual Meeting of the Chemical Society of Japan, Kyoto, April 5, 1956.



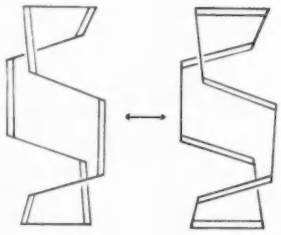
I I'



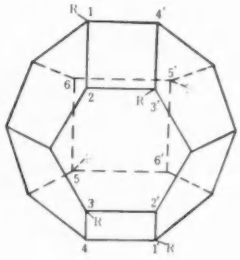
II R=OH ; $C_{20}H_{12}(OH)_8$
III R=H ; $C_{20}H_{20}$



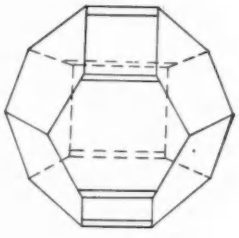
IV $C_{20}H_8$



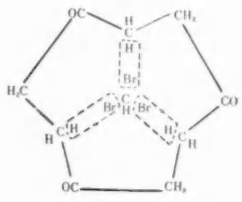
V VA



VI R=OH ; $C_{20}H_{12}(OH)_8$



VII $C_{20}H_8$



VIII

2 will similarly lead to an optically active dimerization product VI (it shall be tentatively named "hexahydroxyisododecahedrane"). The corresponding product from case 3 will be the optical isomer of VI. In both compound VI and its optical isomer not only the cyclobutane rings but also the cyclohexane rings are strongly strained, because the latter may be forced to take an almost coplanar form. Dehydration at the instant of their formation may afford the same optically inactive isododecahedrahexaene $C_{20}H_8$, as shown by formula VII with arbitrary positions of the six double bonds.

Thus *d*, *l*-tricyclone, I+I', may produce dodecahedrahexaene and isododecahedrahexaene along with a large amount of undefinable polymerization products from improper collisions among the tricyclone molecules.

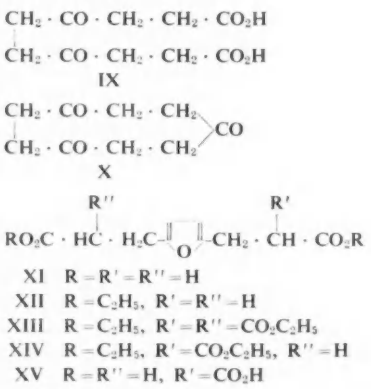
Success depends on our ingenuity in the synthesis of *d*, *l*-tricyclone because we even expect that the tricyclone, if once formed, may condense spontaneously to give hexaene IV, although it may have to be separated from isohexaene VII. When condensed with bromoform, the compound given in the title of this paper, or 1, 4, 7-cyclononatrione (X), may give *d*, *l*-tricyclone accompanied by other condensation products (see VIII). This paper communicates the synthetical efforts paid by us for obtaining cyclononatrione (X). The syntheses of the so-called "medium ring"[1] compounds which are composed of 9, 10 or 11 methylenes are known to be difficult[2]. Some simple compounds among them, however, were synthesized recently by Prelog and Stoll's method[2], and it is especially noteworthy, that these medium ring compounds possess particular

1) H. C. Brown and M. Borkowsky, *J. Am. Chem. Soc.*, **74**, 1894 (1952).
2) V. Prelog, *J. Chem. Soc.*, **1950**, 420.

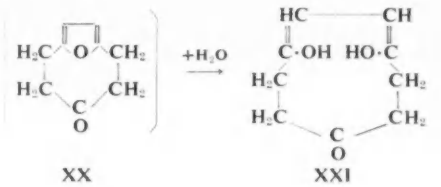
internal strain (transannular effect)[3] when compared with other smaller or larger ring compounds. Apart from the question of transannular effect, there are fears lest cyclononatrione should suffer intramolecular condensation, and yet the first attempt adopted by us lay in the dry distillation of the barium salts of 4, 7-dioxodecanedioic acid (IX) according to Ruzicka's ring ketone syntheses[4]. The acid IX was obtained early by Kehrer et al.,[5] later by Asahina and Fujita[6], and then by Hachihama et al.[7], through hydrolytic furan-ring fission of δ-furfurylidenelevulinic acid.

The acid IX was mixed with barium carbonate and pyrolysis was carried out by heating under reduced pressure. Indeed, a ketone was separated as its semicarbazone (m. p. 184° (decomp.)) from the neutral part of the distillate thus obtained, but the analytical value of its nitrogen content was too small to conclude that the trissemicarbazone of the triketone X was really obtained.

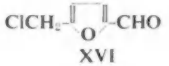
The yield of this undefinable semicarbazone in the above attempt was poor, but the synthesis turned out to be successful by boiling tetraethyl 2, 5-diethylfuran-β, β, β', β'-tetracarboxylate (XIII) or triethyl 2, 5-diethylfuran-β, β, β'-tricarboxylate (XIV) with hydrobromic acid[8]. The compounds XIII and XIV were synthesized by the following scheme.



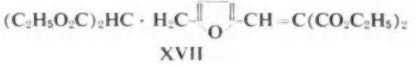
XI R = R' = R'' = H
XII R = C_2H_5, R' = R'' = H
XIII R = C_2H_5, R' = R'' = $CO_2C_2H_5$
XIV R = C_2H_5, R' = $CO_2C_2H_5$, R'' = H
XV R = R'' = H, R' = CO_2H



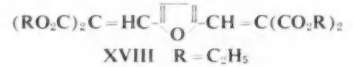
XX XXI



XVI



XVII



XVIII R = C_2H_5
XIX R = H

4, 7-Dioxodecanediocic acid (IX), when heated over its melting point, afforded 2, 5-diethylfuran-β, β'-dicarboxylic acid (XI)[6a),7b)], which was converted into its ethyl ester XII. Introduction of an ethoxycarbonyl group into the β-position of the latter was carried out according to Jone's procedure[9]. From the reaction product, XIV was distilled at 132~155°C/0.15~0.27 mmHg in a poor yield. Without further purification the tarry residue was hydrolyzed with alcoholic potash to give 2, 5-diethylfuran-β, β, β'-tricarboxylic acid (XV) which, was identical with the hydrolysis product of XIV. 5-(Chloromethyl)-furfural (XVI)[10], on the other hand, gave tetraethyl 2-ethyl-5-vinylfuran-β, β, β', β'-tetracarboxylate, (XVII) when treated with diethyl malonate. Catalytic reduction of XVII with platinum black afforded XIII. Neither did the latter distill out even in vacuo nor showed any sign of crystallization. It was immediately hydrolyzed with alcoholic potash, and then acidified with dilute sulfuric acid whereupon XV was obtained. These facts revealed that XIII was produced accompanied by XIV. Since it seemed noteworthy that, in the above-mentioned hydrolysis of XIII, only one ethoxycarbonyl group underwent decarboxylation simultaneously with hydrolysis, two more examples of the hydrolysis of related malonic ester derivatives were carried out. When XVII was shaken with aqueous potassium hydroxide at room temperature for a long time, and the reaction mixture was acidified, one ester group remained unchanged and one of the three hydrolyzed carboxyl groups underwent decarboxylation, thus a mono ester of a tricarboxylic

3) (a) V. Prelog and K. Schenker, *Helv. Chim. Acta*, **36**, 896, 1181 (1953); (b) A. C. Cope et al., *J. Am. Chem. Soc.*, **74**, 5885 (1952); (c) R. Robinson et al., *Chem. & Ind.*, **1953**, 944; (d) N. J. Leonard et al., *J. Am. Chem. Soc.*, **76**, 630, 3463, 5708 (1954).

4) L. Ruzicka et al., *Helv. Chim. Acta*, **9**, 249, 499 (1926); ibid., **11**, 496, 670 (1928).

5) (a) A. Ludwig and E. A. Kehrer, *Ber.*, **24**, 2776 (1891); (b) E. Hofacker and E. A. Kehrer, ibid., **28**, 917 (1895); c) E. Hofacker and E. A. Kehrer, *Ann.*, **294**, 165 (1896).

6) (a) Y. Asahina and M. Fujita, *J. Pharm. Soc. Japan*, **448**, 471 (1919); (b) Y. Asahina and M. Fujita, ibid., **470**, 331 (1931); (c) M. Fujita, ibid., **492**, 67 (1923).

7) (a) I. Hayashi, I. Kumashiro and Y. Hachihama, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), **57**, 299 (1954); (b) I. Hayashi and Y. Hachihama, ibid., **57**, 504 (1954).

8) L. Crombie, J. E. H. Hancok and R. P. Linstead, *J. Chem. Soc.*, **1953**, 3496.

9) V. H. Wallingford, A. H. Homeyer and D. M. Jones, *J. Am. Chem. Soc.*, **63**, 2056 (1941).

10) (a) Org. Syn., **14**, 62 (1934); (b) W. N. Haworth and W. H. H. Jones, *J. Chem. Soc.*, **1944**, 667.

acid (relative positions of its carboxyl and ester groups are ambiguous) was obtained. On the other hand, when tetraethyl 2,5-divinylfuran-$\beta, \beta, \beta', \beta'$-tetracarboxylate (XVIII)[11,12] was hydrolyzed by heating with sodium hydroxide and acidifying with sulfuric acid, 2,5-divinylfuran-$\beta, \beta, \beta', \beta'$-tetracarboxylic acid (XIX) was procured without suffering decarboxylation. Thus the malonic ester derivative (XVIII), in which the α-carbon atoms of the malonic ester groups are connected with α double linkings, undergoes only hydrolysis but not decarboxylation.

Now the tricarboxylic acid ester XIV was heated with 48% hydrobromic acid for 30 min. according to Linstead's method[3]. If ring closure occurred XX should be yielded. Although the compound XX is bicyclic with two double bonds at the bridged heads it may be capable of existence, because one of the two rings is eight-membered, hence belonging to an exceptional case of Bredt's rule[2]. As a matter of fact we could isolate the triketone X (or the keto form of XXI) as its trissemicarbazone (m. p. 176~177°C (decomp.)) from the neutral part of the reaction product, thus indicating the intermediate formation of the hypothetical bicyclic compound XX. In this case, only a little amount of XI was recovered from the acidic part, but the major amount became a black polymer which was rather soluble in water. The yield of the trissemicarbazone of X based on XIV ranged from 2 to 4%. Compounds, corresponding to mono- and bis-semicarbazones, were not detected. When the crude material of XIII was used as the starting material, X was obtained with poorer yields (0.5~1%). When XIV or XII were subjected to Dieckmann's ring closure with sodium and sodium methoxide, no ring formation was observed but XI besides the starting material were yielded.

The attempt to obtain the compound X from its semicarbazone was fruitless. When the trissemicarbazone was treated with alcoholic sulfuric acid, only a tarry matter was obtained as a neutral substance, which neither distilled in high vacuum nor gave any simicarbazone when treated with semicarbazide.

Experimental[13]

Dry distillation of 4,7-dioxodecanedioic acid.—A small saber flask, which was wrapped with a copper wire gauze, was attached to a well chilled trap. 4,7-Dioxodecanedioic acid (5 g., 1 mol.) and barium carbonate (4.3 g., 1 mol.) were powdered and intimately mixed and the whole was put into the flask. The flask was heated in vacuo gently at the beginning but later stronger with a free flame under constant moving. The oily distillate has an allyl-alcohol-like disagreeable smell. This pyrolysis was repeated five times and 25 g. in total of 4,7-dioxodecanedioic acid gave 4.3 g. of the distillate. The distillate was dissolved in ether, washed successively with aqeous sodium bicarbonate, 10% sodium carbonate, and 5% sodium hydroxide, and finally with water, dried and evaporated. The yield of the neutral oily substance was 220 mg. Vacuum distillation gave a colorless oil, b. p. 205~248°C/0.1~0.14 mmHg; yield, 110 mg. Its semicarbazone was obtained in an usually way. Recrystallization from chloroform gave grayish white platelets, m. p. 184°C (partly decomp.).

Found: C, 42.68; H, 7.67; N, 34.70. Calcd. for $C_{12}H_{21}N_9O_4$: C, 42.47; H, 6.24; N, 37.15%.

Acidification of the aqueous sodium bicarbonate solution with sulfuric acid gave 50 mg. of an acidic material, m. p. 141~146°. The latter (28 mg.), without further purification, was titrated with 0.098 N sodium hydroxide, 2.8 cc. being consumed. When calculated for a dibasic acid its molecular weight is 230. This value roughly corresponds to that for 2,5-diethylfuran-β, β'-dicarboxylic acid (XI) (m. p. 155°C with partial decomp., molecular weight 212). The sodium carbonate washing was acidified with dil. sulfuric acid and then shaken with ether. The ethereal solution, when evaporated, left an oily substance with strong phenolic smell. The sodium hydroxide washing behaved quite similarly. The phenolic oils of the two origins were therefore combined (250 mg. in total) and treated with *p*-nitrobenzoyl chloride. A small amount of crystals with m. p. 86~91°C was obtained but both its purity and quantity were insufficient for micro analysis.

Diethyl 2,5-diethylfuran-β, β'-dicarboxylate (XII) and Diethyl 4,7-dioxodecanedioate—A mixture of 2,5-diethylfuran-β, β'-dicarboxylic acid (XI, 45 g.), absolute alcohol (300 cc.), benzene (150 cc.) and 2 drops of conc. sulfuric acid was subjected to azeotropic distillation. When the main bulk of alcohol distilled out further azeotropic distillation was repeated twice, with the addition of alcohol (100 cc.) and benzene (30 cc.) each time. Then the solvent was removed as much as possible. The residue was dissolved in ether, and the solution was washed successively with aqueous sodium bicarbonate and water, dried and evaporated. Vacuum distillation gave 36 g. (63%) of a colorless liquid, b. p. 155~161°C/4 mmHg. Redistillation gave XII in analytical purity as a liquid of b. p. 147~148°C/3 mmHg.

Found: C, 62.62; H, 7.58. Calcd. for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

During the above written manipulation of vacuum distillation the distillate over 180°C/4 mmHg. solidified in the condenser, and the residue in the distilling flask also solidified. Combined yield, 8 g. (13%). Recrystallization from petroleum ether (b. p. 40~55°C) gave diethyl 4,7-dioxodecanedioate[5b] as colorless scales, m. p. 46~46.5°C. No melting point depression was observed, when mixed with an authentic specimen.

11) W. F. Cooper and W. H. Nuttall, *J. Chem. Soc.*, **101**, 1074 (1912).
12) W. F. Cooper and W. H. Nuttall, ibid., **105**, 2218 (1914).
13) All melting points are uncorrected.

Found: C, 58.77; H, 7.75. Calcd. for $C_{14}H_{22}O_6$: C, 58.73; H, 7.75%.

Triethyl 2,5-diethylfuran-β,β,β'-tricarboxylate (XIV).—The above compound XII (13 g., 1 mol.) and diethyl carbonate (75 g., 6 mol.) were mixed well in a 500 cc. distilling flask, and to the mixture was slowly added a sodium ethoxide solution [2.3 g. metallic sodium in absolute alcohol (70 cc.)] with stirring. The solution gradually changed to pinkish yellow in color and yielded gray precipitates. Alcohol was removed slowly and carefully in a water bath. Dry benzene (30 cc.) was then added, and the solvent was removed by distillation as much as possible first on a steam bath, finally in an oil-bath (160~170°C) in vacuo. After cooling water was added, the residue was acidified with sulfuric acid, and extracted with ether. The ethereal solution was washed with water, dried and evaporated. High vacuum distillation gave 3.3 g. (20%) of an oil which solidified on standing. B. p. 132~135°C/0.15~0.27 mmHg. Recrystallization from petroleum ether (b. p. 35~45°C) with exterior cooling in dry ice gave XIV as colorless platelets, m. p. 28~29°C.

Found: C, 60.29, H, 6.85. Calcd. for $C_{17}H_{24}O_7$: C, 56.99; H, 7.10%.

Tetraethyl 2,5-diethylfuran-$\beta,\beta,\beta',\beta'$-tetracarboxylate (XIII).—5-(Chloromethyl)-furfural (XVI, b. p. 137~138°C/5 mmHg, 16 g., 1 mol.) was added with cooling, to an alcoholic solution of magenesium salt of diethyl malonate [magnesium (2.5 g., 1 atom) dissolved in diethyl malonate (17 g., 1 mol.)]. The whole was kept standing at room temperature, and then refluxed for 1 hr. To this solution were added diethyl malonate (17 g., 1 mol.) and piperidine (0.5 cc.), and the whole was refluxed for 7.5 hr. The solvents were evaporated as thoroughly as possible, and then water was added to the risidue. After acidification with sulfuric acid, the reaction mixture was extracted with ether, washed with water and dried. Removal of the ether gave XVII as a dark red viscous oily substance which did not crystallize nor distil out on high vacuum distillation. The identification was carried out by way of its hydrolysis product (described later). An alcoholic solution (100 cc.) of the crude material of XVII (4.2 g., 0.1 mol.) was subjected to catalytic hydrogenation with platinum black (0.2 g.) as the catalyst, thereby 186 cc. (0°C, 760 mmHg; 0.085 mol.) of hydrogen gas being consumed during 60 min. Filtering off the catalyst and subsequent evaporation of alcohol gave a very viscous oily substance (XIII), its purification being fruitless.

2,5-Diethylfurane-β,β,β'-tricarboxylic acid (XV).—a) From XIV: A solution of XIV (3 g.) in 20% aqueous sodium hydroxide (50 cc.) was heated on a steam bath for 1 hr. The whole was acidified with sulfuric acid under cooling, salted out with table-salt, and extracted with ether. The ethereal layer was washed with water, dried and evaporated. The residue, after digestion with hot water (1 cc.), was allowed to stand for 2 or 3 days, thus yielding a little amount (0.3 g.) of crystals. Recrystallization from aqueous methanol afforded XV as colorless platelets, m. p. 102~105°C (decomp.).

Found: C, 48.66; H, 5.32. Calcd. for $C_{11}H_{12}O_7 \cdot H_2O$: C, 48.18; H, 5.15%.

An aqueous solution of the above-obtained substance (0.265 g.) was titrated with 0.102 N aqueous sodium hydroxide, phenolphthalein being used as an indicator.

Found: 30.2 cc. Calcd.: 28.4 cc.

b) From XIII: Hydrolysis of the crude material XIII, already described above, gave the same XV.

Hydrolysis of Tetraethyl 2-ethyl-5-vinylfuran-$\beta,\beta,\beta',\beta'$-tetracarboxylate (XVII).—The benzene (5 cc.) solution of the crude material of XVII (15 g.) was shaken with 20% aqueous potassium hydroxide (100 cc.) for 17 hr. at room temperature, then the whole was acidified with sulfuric acid under ice-cooling, and was extracted with ether. The ethereal layer was washed with water, dried and evaporated, thus a colorless solid matter (1 g.) was obtained. Recrystallization from wet benzene gave colorless plates, which melt at 148.5~149°C with decomposition. Elementary analysis as well as titration revealed, that this compound ($C_{13}H_{14}O_7 \cdot \frac{1}{2}H_2O$) may be derived from XVII through hydrolysis. Simultaneous decarboxylation occurred in any one of the four ethoxycarbonyl groups contained in the molecule of XVII.

Found: C, 53.40; H, 5.67. Calcd. for $C_{13}H_{14}O_7 \cdot \frac{1}{2}H_2O$: C, 53.61; H, 5.91%.

The above-mentioned substance (0.301 g.) was titrated with 0.102 N aqueons sodium hydroxide, giving the following results.

Found: 22.1 cc. Calcd.: 19.6 cc.

2,5-Divinylfuran-$\beta,\beta,\beta',\beta'$-tetracarboxylic Acid (XIX).—Tetraethyl 2,5-divinylfuran-$\beta,\beta,\beta',\beta'$-tetracarboxylate (XVIII) (2 g.), which had been obtained by Cooper's method[12], was dissolved in 27% aqueous sodium hydroxide (50 cc.) and the whole was heated on a steam bath for 1 hr. The solution was then acidified with sulfuric acid, salted out with table-salt, and then extracted with ether. The ethereal layer was washed with water, dried and evaporated. The residue was dissolved in hot water (1 cc.) and then kept in a vacuum desiccator. Crystals which appeared during 10 days were collected, and recrystallized from ethyl acetate and then from hot water. Orange red plates, m. p. 218°C (decomp.); yield, 0.5 g. (39%).

Found: C, 46.01; H, 3.39. Calcd. for $C_{12}H_8O_8 \cdot H_2O$: C, 45.87; H, 3.21%.

The above-mentioned substance (0.317 g.) was titrated with 0.102 N aqueous sodium hydroxide, giving the following result.

Found: 40.5 cc. Calcd.: 39.0 cc.

Trissemicarbazone of 1,4,7-cyclononatrione (X).—The tricarboxylic acid triester XIV (5 g.) was mixed with 48% hydrobromic acid (30 cc.) and the whole was refluxed gently for 30 min. After cooling, the dark solution which occasionally contained a black solid matter was treated with water (100 cc.) and ethyl acetate. The ethyl acetate layer was washed successively with water, aqueous sodium bicarbonate, and finally with water, and dried. Removal of the solvent gave a dark orange liquid. Semicarbazone was obtained by the usual method as a gray solid (0.1~0.2 g.), which, when recrystallized from methanol or alcohol, underwent decomposition. Recrystallization from benzene—although the solubility in it was small—gave grayish

white plates, m. p. 176~176.5°C (partly decomp.); yield, 30 mg.

Found: C, 42.08; H, 7.00; N, 36.79. Calcd. for $C_{12}H_{21}O_3N_9$: C, 42.47; H, 6.24; N 37.15%.

The aforesaid washings with aqueous sodium bicarbonate were acidified with sulfuric acid, yielding a grayish white solid. Recrystallization from water gave IX, m. p. 155~156° (partly decomp.). The black polymer, obtained in this reaction, was rather soluble in water, very soluble in alcohol or acetone, but insoluble in ether and ethyl acetate. Further investigation was given up, since the attempts of purification failed.

Since one of us (Kawai) must now give up his laboratory life, in consequence of his personal circumstance, we hope that anyone who feels interested in this field will persue the synthetical attack on the "dodecahedrane", the existence of which is theoretically possible.

We are indebted to the Ajinomoto Co. for the gifts of valuable compounds for the present research. Thanks are also due to the Science Research Institute and the Takamine Kenkyusho in the Sankyo Co. for microanlyses.

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Bromination of Ethyl Diacetosuccinate

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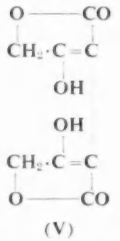
Although the synthesis of 1, 4, 7-cyclononatrione has been realized by us[1], it was isolated only as its trissemicarbazone in a poor yield. We have now chosen another course to attain this cyclic triketone, thus intending at first to obtain ethyl 1, 4, 7-cyclononatrione-2, 3, 6, 8-tetracarboxylate through the condensation of γ,γ'-dibromodiacetosuccinate (II) and ethyl disodioacetonedicarboxylate. This attempt, however, failed presumably owing to the false constitution (II) of the so-called γ,γ'-dibromodiacetosuccinate. Consequently, the bromination of ethyl diaceto succinate (I) had to be reinvestigated and the present paper presents some new aspects as an exceptional example of the bromination of β-ketoesters.

Informations concerning II can be summarized as follows: Wolff et al.[2] treated ethyl diacetosuccinate (I) with two moles of bromine and ascribed formula II to the pale yellow reaction product because of the fact that the substance in question, when heated at 150~160°C, gave bistetronic acid (V) by giving up two moles of ethyl bromide. On the other hand, Hirst et al. treated the same bromination product with hydrazine and concluded from the estimation of the nitrogen gas evolved that the bromide was a mixture of 21% of α,α'-dibromo compound III and 79% of γ,γ'-dibromo compound II[3], in other words, an equilibrium mixture due to an α,γ-shift of bromine atoms[3-5].

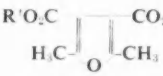
$RCH_2 \cdot CO \cdot CR' \cdot CO_2C_2H_5$

$RCH_2 \cdot CO \cdot CR' \cdot COC_2H_5$

(I) R = R' = H
(II) R = Br, R' = H
(III) R = H, R' = Br
(IV) R = R' = Br



(V)



(VI) R = H, R' = C_2H_5
(VII) R = R' = H
(VIII) R = R' = CH_3
(IX) R = R' = C_2H_5

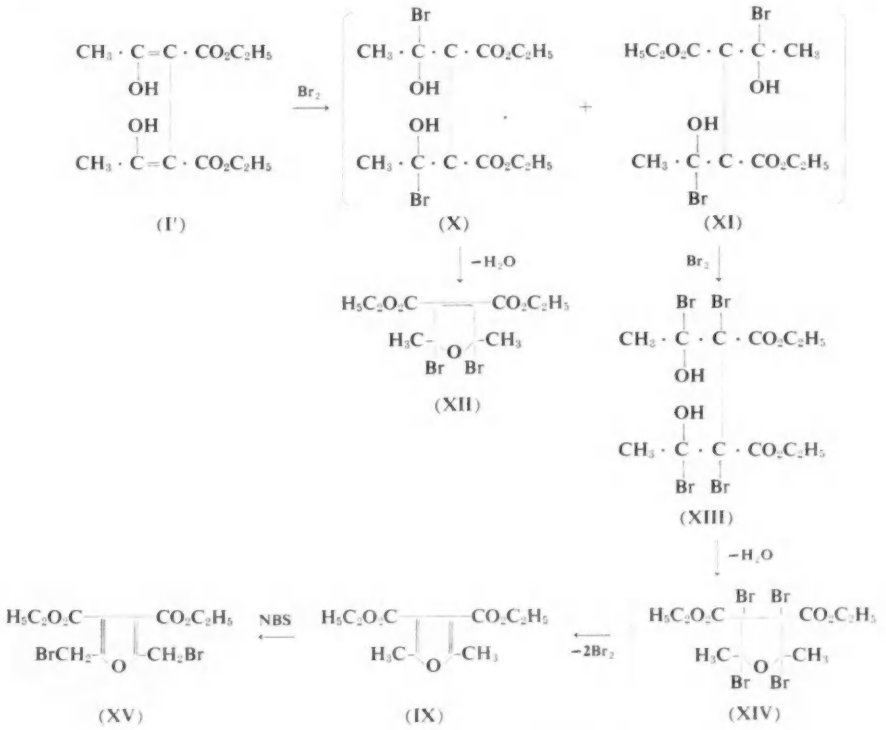
In fact, we could obtain a pale orange yellow viscous oil without hydrogen bromide evolution when we brominated compound I after Wolff's method[2], but the vacuum distillation of this

1) S. Kawai, S. Tanaka, K. Terai, M. Tezuka and T. Nishiwaki, This Bulletin, 33, 669 (1960).
2) L. Wolff and H. Junker, *Ann.*, 399, 311 (1913).
3) E. L. Hirst and A. K. Macbeth, *J. Chem. Soc.*, 121, 2169 (1922). Their conclusion was deduced from the fact that the bromine atom of the α-bromide is so reactive that it decomposes hydrazine with the evolution of nitrogen gas quantitatively but the γ-bromide remains intact.
4) (a) C. Duisberg, *Ann.*, 213, 137 (1882). (b) A. Hantsch, *Ber.*, 27, 356, 3168 (1894). (c) M. Conrad, ibid., 29, 1024 (1896). (d) A. K. Macbeth and D. Trail, *J. Chem. Soc.*, 127, 1118 (1925). (e) M. S. Kharasch, E. Sternfeld and F. R. Mayo, *J. Am. Chem. Soc.*, 59, 1655 (1937). (f) F. Kröhnke and H. Timmler, *Ber.*, 69, 614 (1939).
5) A. Becker, *Helv. Chim. Acta*, 32, 1114, 1584 (1949).

oil gave only a little amount of a distillate at 150~170°C (bath temperature) and then met with a sudden rise of the pressure obviously due to decomposition. The distillate contained monoethyl 2, 5-dimethylfuran-3, 4-dicarboxylate (VI), and the residue included 2, 5-dimethylfuran-3, 4-dicarboxylic acid (VII) as one of its constituents.

Then, we gave up vacuum distillation, and kept the viscous oily bromination product of compound I (it shall be called "I-bromide" hereafter) in a cool place during one month. Crystals which gradually appeared in the meanwhile were collected at appropriate intervals and at least four new compounds, i.e. I-tetrabromide (XIII), monoester VI, dicarboxylic acid VII and the dibromide of diester IX, were isolated.

The I-bromide gave neither any indole derivative when heated with a mixture of aniline and aniline hydrobromide[6], nor a *p*-nitrophenylpyridazine derivative when treated with *p*-nitrophenylhydrazine[6]. These results show the absence of a γ,γ'-dibromide such as II or IV. Since the I-bromide, when heated with resorcinol or with α-naphthol, did not give any bromophenol or bromonaphthol, the bromine atom is not so "positive"[7]. Thus the presence of α,α'-dibromide derivatives such as III or IV is excluded. The I-bromide, when heated with absolute methanol, gave dimethyl 2, 5-dimethylfuran-3, 4-dicarboxylate (VIII), and a desmotropic form[8] of diacetosuccinic acid (I, H instead of C_2H_5) when heated with sodium methoxide. When treated with concentrated sulfuric acid[5,9] the I-bromide did not show any sign of a ketonic hydrolysis but gave the free acid VII. The I-bromide gave no definite product when heated with aqueous potassium carbonate[10]. On the other hand, compound I gave diethyl 2, 5-dimethylfurandicarboxylate (IX) on treatment with concentrated sulfuric acid and acetonylacetone on heating with aqueous potassium carbonate, both in good yields. When hydrogen bromide gas was passed through a benzene solution of compound I, only a very little



6) J. R. Catch and E. R. H. Jones, *J. Chem. Soc.*, **1948**, 272, 276.

7) R. Altschul and P. B. Bartlett, *J. Org. Chem.*, **5**, 623 (1942).

8) Thirteen isomeric forms are theoretically possible for diacetosuccinic acid, but only three are known [L. Knorr, *Ber.*, **22**, 170 (1889); *Ann.*, **293**, 103 (1896)]. The compound obtained above does not agree in the melting point with any of the three.

9) P. Ruggli, A. von Wartburg and H. Erlenmeyer, *Helv. Chim. Acta*, **30**, 348 (1947).

10) L. Knorr, *Ber.*, **33**, 1219 (1900).

amount of VII was obtained and the major part of compound I remained unchanged. Therefore, the two compounds, VI and VII, which were isolated from the I-bromide, should never have been derived from the starting material (I) through the catalytic action of the little amount of hydrogen bromide generated during the bromination of compound I.

As has already been mentioned, there is no positive proof for the existence of α,α'-dibromide III and γ,γ'-dibromide II. Hence, the elucidation of the constitution of the I-tetrabromide, found as one constituent of I-bromide, appeared difficult. We are now forced to assume that the dienediol form I' of compound I gave a mixture of *cis*-dibromide X and *trans*-dibromide XI as the result of 1, 4-addition of bromine, and the former (X) passed over to a dihydrofuran XII while the latter (XI) took up another mole of bromine to produce tetrabromide XIII. Then, tetrabromide XIII underwent dehydration catalyzed by hydrogen bromide, thus yielding a tetrabromide XIV, which, as the result of spontaneous debromination, gave furan derivative IX. Compound IX suffered partial and total hydrolysis catalyzed by hydrogen bromide, yielding compounds VI and VII. The precise structure of dibromide XII is further shown by the fact that it is quite different from dibromide XV obtained from the dimethylfuran derivative IX through *N*-bromosuccinimide. Thus, the I-tetrabromide in question may perhaps be represented by formula XIII, because this compound is so unstable that it decomposes (dehydration?) when merely heated or treated with water-miscible solvents.

The proof that the main course involved in this reaction belongs to bromine addition but not bromine substitution can be found in the following facts: (i) during the bromination of compound I evolution of hydrogen bromide was scarcely recognized: (ii) on the other hand, hydrogen bromide evolution was observed during the manipulation of recrystallization of crystals gathered from the I-bromide.

Both Wolff[1] and Hirst[2] observed that bromine substitution took place when ethyl diacetosuccinate was treated with bromine, which does not agree with our experiments. Our observation seems more reasonable, because the more stable conjugated dienediol-form I' may predominate over the unconjugated diketo-form I in ethyl diacetosuccinate, and the reaction may start with the 1, 4- and further 2, 3-addition of bromine to the conjugated system but not with bromine substitution.

Experimental[11]

Bromination of Ethyl Diacetosuccinate.—To a solution of ethyl diacetosuccinate[12] (I) (140 g., 1 mol.) in chloroform (300 cc.) bromine (170 g., 1.95 mol.) was added dropwise in 2 hr. with ice-cooling and stirring, and the mixture was stirred for 2 hr. at room temperature. Hydrogen bromide was scarcely evolved, or estimated as only 0.53% of the value calculated for bromine substitution. The chloroform layer was washed successively with water, with 5% sodium thiosulfate and finally with water, dried and evaporated in vacuo on a water bath (below 38°C), giving "I-bromide" as a pale reddish orange substance containing a small amount of colorless crystals. Yield, 290 g.

I-Tetrabromide (XIII) of Ethyl Diacetosuccinate.—The small amount of colorless crystals, obtained above, were separated from the oily substance, washed with a small amount of petroleum ether (b. p. 40~50°C), dried and recrystallized from anhydrous benzene to yield the I-tetrabromide as colorless plates, m. p. 189°C (decomp.). Yield, 1.2g.

Found: C, 25.15; H, 2.59; Br, 55.83. Calcd. for $C_{12}H_{14}O_6Br_4$: C, 24.94; H, 3.14; Br, 55.31%.

When the above oily substance was left to stand, further crops of XIII were obtained during 2 or 3 days. The total yield was 2.7 g. On long heating in an attempt to recrystallize from aqueous benzene or anhydrous benzene, XIII changed to an indefinite substance with evolution of hydrogen bromide. On the other hand, when a water-miscible solvent such as methanol, alcohol and acetone, were used, XIII changed to VII.

Separation of VI, VII and XII from "I-Bromide".—When XIII was separated from the "I-bromide", and the oily substance was left to stand, crystals gradually separated out during 5~30 days. Addition of a small amount of ether promoted crystallization. Since the collection of the crystals by filtration was quite difficult because of the viscousness of the liquid, the whole was placed on a porcelain plate in spite of the loss of the yield or diluted with ether and then filtered. The solid thus obtained showed various melting points such as m. p. 60~90°C, m. p. 110~115°C (decomp.) and m. p. 130~140°C (partly decomp.), and was a mixture of VI, VII, XII, XIII and I as described below. When the oily substance was kept on standing for more than 3 months, hydrogen bromide and bromine were evolved gradually, yielding a solid which was mainly VII.

The solid obtained above was dissolved in anhydrous benzene, and then an insoluble substance was filtered off. The most soluble part was left to stand, a small amount of crystals being formed in the meanwhile. Filtration and recrystallization from petroleum ether (b. p. 40~50°C) gave VI[13] as colorless long plates, m. p. 83~84°C.

Found: C, 56.60; H, 5.83. Calcd. for $C_{12}H_{12}O_5$: C, 56.60; H, 5.70%.

The filtrate from VI was evaporated, yielding another crystalline substance. Recrystallization from petroleum ether (with active carbon) gave

11) All melting points are uncorrected.

12) (a) E. Fischer, "Anleitung zur Darstellung organischer Präparate", Berlin, Friedrich Vieweg u. Sonn. (1922), p. 48. (b) L. Knorr and F. Haber, *Ber.*, **27**, 1155 (1894). (c) L. Knorr, *Ann.*, **306**, 332 (1899).

13) (a) G. H. U. Harrow, *Ann.*, **201**, 152 (1880). (b) L. Knorr, *Ber.*, **17**, 2864 (1884); ibid., **22**, 153 (1889).

unchanged I as colorless scales, m. p. 92～93°C, which was identified by mixed melting point determination.

Found: C, 55.86; H, 6.98. Calcd. for $C_{12}H_{19}O_6$: C, 55.80; H, 7.03%.

When the crystals, separated from the part soluble in benzene, were recrystallized from anhydrous benzene, XII was obtained as colorless long pillars, m. p. 92～96°C (decomp.). It melted at 92～96°C with decomposition to a substance which melted at 128～130°C and gave the positive Beilstein halogen test.

Found: C, 36.20; H, 3.59. Calcd. for $C_{12}H_{16}O_5Br_2$: C, 36.03; H, 4.03%.

From the part more soluble in benzene than XII, a small amount of XIII, previously mentioned, was obtained.

From the part less soluble than XII and from the first insoluble part, a crude material of VII was obtained. During recrystallization XII partly changed to VII, and use of recovered benzene promoted the change. The latter was collected and recrystallized from aqueous methanol or water, yielding VII as colorless pillars of m. p. 234～236°C (partly decomp.).

Found: C, 49.70; H, 4.77. Calcd. for $C_5H_5O_5 \cdot \frac{1}{2}H_2O$: C, 49.74; H, 4.70%.

The yields of VI, I, XII and VII were 2.2 g., 0.8 g., 1.7 g. and 28.5 g., respectively.

Vacuum Distillation of "I-Bromide". — After removal of XIII, "I-bromide" (50 cc.) was heated under the reduced pressure of 5～6 mmHg. The pressure dropped to 30～40 mmHg at 150～170°C (bath-temperature) and again rose to 6～7 mmHg after 10 min. A pale orangish oily substance distilled out at ca. 200°C (bath-temperature). When the distillate was triturated with a small amount of ether, it solidified. Recrystallization from aqueous methanol gave VI as colorless long pillars of m. p. 83～84°C, b. p. 100～105°C/0.25～0.3 mmHg. Yield, 2.1 g. It was identified by a mixed melting pont with an authentic sample.

The residue was a very viscous reddish black syrup containing a small amount of a solid and had a distinct smell of hydrogen bromide and bromine. To the residue a small amount of ether was added, and the whole was kept standing in a stoppered flask for 2 or 3 days, yielding crystals gradually. These were collected on a filter and recrystallized from aqueous methanol (1 : 1) to give VII as colorless pillars, m. p. 234～236°C (partly decomp.). Yield, 3.8 g.

Hydrolysis of VI.—VI (1.2 g.) was dissolved in alcohol (60 cc.), and 50% sulfuric acid (5 cc.) was added, and the whole was refluxed for 4 hr. After removal of the alcohol, water was added. The precipitate, which formed in the meanwhile, was recrystallized from water, giving VII, m. p. 234～235°C (partly decomp.).

Reaction of "I-Bromide" with Methanol.—1) The oily "I-bromide" (2 g.), freed from all the crystals VI, VII, XII and XIII, was mixed with absolute methanol, and the whole was refluxed on a steam bath for 5 hr. After cooling a small amount of crystals were yielded. Recrystallization from water gave VII. The methanolic filtrate from VII was concentrated, giving first a small amount of a colorless substance of m. p. 100～110°C. Recrystallization from petroleum benzine (b. p. 60～75°C) gave colorless long pillars of m. p. 118～119°C, the amount being too little to be analyzed. From the last portion of the methanolic filtrate, colorless long plates of m. p. 45～46°C were obtained. Recrystallization from petroleum ether (b. p. 40～50°C) gave VIII[14] as colorless tetragonal plates, m. p. 58～61°C.

Found: C, 56.53; H, 5.70. Calcd. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70%.

2) The mixture of the oily "I-bromide" (2 g.), freed from all the crystals, with sodium methoxide (sodium 0.2 g., absolute methanol 50 cc.), was refluxed on a steam bath for 2 hr., and after the methanol was removed as much as possible and water was added, it was acidified with sulfuric acid to yield a white residue. Recrystallization from benzene (with active charcoal) gave a compound of m. p. 120～121°C (partly decomp.) as pale yellow plates, which were analyzed as diacetosuccinic acid.

Found: C, 47.59; H, 4.94. Calcd. for $C_8H_{10}O_6$: C, 47.53; H, 4.99%.

Hydrolysis of "I-Bromide".—1) The oily "I-bromide" (1 g.) freed from all the crystals was treated with concentrated sulfuric acid (5 cc.) and the whole was heated on a steam bath for 1 hr. Addition of water yielded grayish white precipitates, which, on recrystallization from benzene and then water, gave VII.

2) The oily "I-bromide" (6 g.) freed from all the crystals was dissolved in aqueous potassium carbonate (protassium carbonate 7 g., water 25 cc.) and the whole was boiled for 2 hr. After addition of water, the whole was acidified with sulfuric acid, and extracted with ether. The ethereal solution was washed with water, dried and evaporated, leaving a grayish white solid (0.2 g.). Recrystallization from ethylene chloride gave a material of m. p. 176～180°C (decomp.), which was not analyzed because of the impurity.

Cyclization of I by Hydrogen Bromide.—Through a cooled solution of I (12 g.) in anhydrous benzene (150 cc.) dried hydrogen bromide was passed for 30 min. The whole was placed in a stoppered flask, and kept standing overnight, yielding crystals. These were recrystallized from aqueous methanol to give 0.7g. of VII. When the benzene filtrate was concentrated, 8.5 g. of I was recovered and a small amount of colorless needles of m. p. 105～112°C were obtained, which could not be further investigated because of the scarcity of the sample.

Ethyl 1-*p*-Nitrophenyl-3, 6-dimethyl-1, 4-dihydropyridazine-4, 5-dicarboxylate (Anhydro-*p*-nitrophenylhydrazone of I).—A solution of I (2 g.) and *p*-nitrophenylhydrazine (1 g.) in 70% acetic acid, was kept standing for 1 hr. at room temperature. The crystals which were yielded were recrystallized from ethyl acetate, giving pale yellow long pillars, m. p. 122～123°C.

Found: N, 11.57. Calcd. for $C_{15}H_{21}O_6N_3$: N, 11.20%.

14) I. M. Heilbron, E. R. H. Jones, P. Smith and B. C. L. Weedon, *J. Chem. Soc.*, **1946**, 57.

Ethyl 2, 5-Di(bromomethyl)furan-3, 4-dicarboxylate (XV).—To a mixture of IX (9.6 g., 1 mol.), *N*-bromosuccinimide (14.3 g., 2 mol.) and carbon tetrachloride (100 cc.), benzoyl peroxide (ca. 0.1 g.) was added. The whole was refluxed gently on a steam bath for 5 hr and allowed to cool. Succinimide which separated was filtered off. The filtrate was concentrated, and the residue was distilled in vacuo, giving XV as a pale yellow, very viscous syrup of b. p. 170~180°C/3 mmHg. Yield, 14.5 g. (91%). When kept standing in an icebox, it solidified, but melted partly at room temperature. The solidified substance was recrystallized from petroleum ether (b. p. 40~50°C) (the solution was kept standing in an icebox to crystallize), giving XV as colorless long plates, m. p. 52~52.5°C.

Found: C, 36.13; H, 3.62. Calcd. for $C_{12}H_{14}O_5Br_2$: C, 36.19; H, 3.52%.

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Near Ultraviolet Absorption Spectra of Acrolein and Crotonaldehyde

By Kōzō INUZUKA

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Near ultraviolet absorption spectra of a number of aldehydes and ketones have been studied by many workers[1]. It is well known that these compounds have a weak absorption in 33300~25000 cm^{-1} region, and that this absorption arises from the transition of an electron from a non-bonding orbital to an excited orbital. We have also studied recently the effects of solvents on the near ultraviolet absorption spectra of some conjugated aldehydes and ketones[2]. In order to study the electronic properties of the carbonyl group in these molecules, we treated in this paper acrolein and crotonaldehyde which have conjugated systems. E. Eastwood and C. P. Snow[3] carried out a vibrational analysis for the n-π^* absorption spectrum of acrolein. The purpose of the present paper is to analyze the n-π^* absorption bands of acrorlein and crotonaldehyde, and also to estimate the amount of elongation of the C=O bond of these molecules during the n-π^* transition from the relative intensities of the C=O progression bands using the method of J. A. Howe and J. H. Goldstein[4].

Experimental

Acrolein and crotonaldehyde (Tokyo Kasei G. R. grade) were distilled before the experiment.

Carbon tetrachloride used as a solvent was boiled with dilute alkali several times. The carbon disulfide free solvent thus obtained was then washed several times with water, dried over phosphorus pentoxide, and distilled. Absorption spectra were measured by a Hitachi E. P. S. double beam automatic recording spectrometer. The absorption cell of 10 or of 40 cm. was used, depending upon the vapor pressure of the sample. All the absorption measurements were made at room temperature. Solution spectra were obtained with 1 cm. cell. For the purpose of checking that the transition in this region is of the n-π^* type, the effects of solvent on the absorption spectra were also studied by changing the solvent from carbon tetrachloride to ethanol.

Result and Discussion

Both of the compounds have weak absorption in 33300~25000 cm^{-1} region in solution and vapor states. In carbon tetrachloride solution each of the absorption spectra exhibits four distinct shoulders. On addition of ethanol

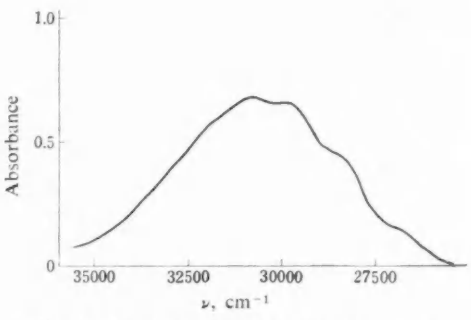

Fig. 1. Spectrum of acrolein in carbon tetrachloride solution.

1) For example, H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941); J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).
2) M. Ito, S. Inuzuka and S. Imanishi, *J. Am. Chem. Soc.* 82, 1317 (1960).
3) E. Eastwood and C. P. Snow, *Proc. Roy. Soc.*, **149A**, 446 (1935).
4) J. A. Howe and J. H. Goldstein, *J. Am. Chem. Soc.*, **80**, 4846 (1958).

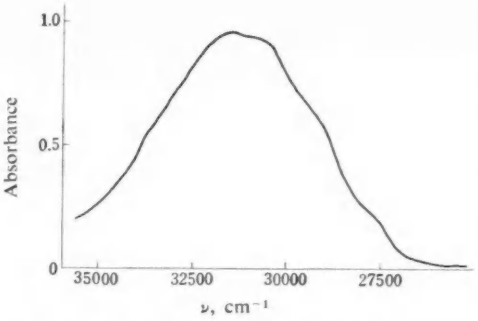

Fig. 2. Spectrum of crotonaldehyde in carbon tetrachloride solution.

to carbon tetrachloride solution the absorption shifts towards shorter wavelengths, and in pure ethanol solution the acrolein maximum shifts to the shorter wavelengths, by 400 cm^{-1} compared with the pure carbon tetrachloride solution. In the case of crotonaldehyde also the blue-shift of 900 cm^{-1} was observed. These blue-shifts indicate the n-π^* nature of the electronic transition.

In the vibrational analysis of the vapor spectrum of acrolein we have taken the strong band at 25873 cm^{-1} as the 0—0 band, which is accompanied on its lower frequency side by three very weak bands at 24647, 24912 and 25555 cm^{-1}. From the higher frequency region of the 0—0 band, we may pick out three vibrational frequencies of 1427, 1271 and 498 cm^{-1} all of which forming long progressions. The progression formed by 1271 cm^{-1} frequency is the most prominent feature in the spectrum. For crotonaldehyde, the 0—0 band taken at 26518 cm^{-1} which is accompained by no prominent band on its lower frequency side. On the high freguency side there are three progressions with the separations of 1360, 1237 and 450 cm^{-1}, respectively, the one with the 1237 cm^{-1} separation being the strongest. For acrolein, E. Eastwood and C. P. Snow[5] found two fundamental vibrational frequencies 1260 and 500 cm^{-1} of the excited state. They assigned the former to the C=O stretching vibration and the latter to an oscillation of the methylene group about the C=C double bond. As it is well known that in ketone and aldehyde n-π^* spectra the C=O stretching vibration generally gives rise to the main progression, the frequencies 1271 cm^{-1} in acrolein and 1237 cm^{-1} in crotonaldehyde may be assigned to the C=O stretching vibration in their excited states. Futhermore, since vibrational modes involving the motion of hydrogen generally do not appear prominently in the electronic spectra it seems to be more reasonable that the 498 cm^{-1} in acrolein and the 450 cm^{-1} in crotonaldehyde should be assigned to the skeletal bending modes instead of the assignment otherwise made by E. Eastwood and C. P. Snow. The frequencies 1427 cm^{-1} of acrolein and 1360 cm^{-1} of crotonaldehyde may be assigned to the C=C stretching vibration in the excited state, corresponding to the ground state vibration frequencies 1618[5] cm^{-1} and 1642[6] cm^{-1}, respectively, observed in Raman spectra. The blue-shift by 645 cm^{-1} of the 0-0 band of crotonaldehyde relative to that of acrolein is in accordance with the fact that the methyl substitution generally leads to the blue-shift of the n-π^* absorption[7,8].

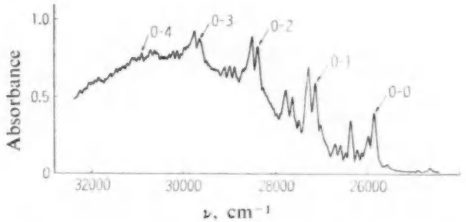

Fig. 3. Absorption spectrum of acrolein vapor.

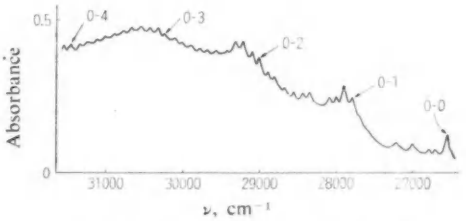

Fig. 4. Absorption spectrum of crotonaldehyde vapor.

In order to check the above assignments, the relative intensities of the member bands in the main C=O progression were calculated with the method used by Hose and Goldstein[4] and were compared with the observed intensities*. Figs. 3 and 4 show the vapor spectra of acrolein and crotonanldehyde. The procedure of this calculation was detailed by D. P. Craig[9]. The C=O group in the molecle was assumed to be a simple diatomic moleclue harmonically bound. The intensity of the 0-n band is given by

5) P. Lambert and J. Lecomtte, *Compt. rend.* **208**, 740 (1939).
6) K. W. F. Kohlrausch und A. Pongratz, *Z. physik. Chem.*, **B27**, 176 (1934).
* The intensity of a band was assumed here to be proportional to the observed optical density value. The intensity contribution from satellite bands was assumed to be the same for all the bonds forming the C=O progression.
7) H. Baba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **72**, 341 (1951).
8) L. E. Orgel, *J. Chem. Soc.*, 121 (1955).
9) D. P. Craig, ibid., 2146 (1950).

$$I_n = (\omega_n/\omega_0)\left[\int \psi_0(\xi_1)\psi_n(\xi_2)\mathrm{d}\tau\right]^2$$

where $\psi_i(\xi_j)$ is the i-th simple harmonic oscillator wave function of the j-th electronic state, and ω_n is a frequency of the n-th band in the progression. Craig has given a formula for evaluating the overlap integral as a function of the separation of the origins of coordinate q of the two reduced oscillators in the electronic states 1 and 2, and also as a function of the ratio of frequencies $\rho = \nu_1/\nu_2$ where ν_1 and ν_2 are the C=O stretching frequencies in the ground and excited states.

The results of calculation for acrolein and crotonaldehyde are shown in Tables I and II. As seen in these tables, calculated intensities for acrolein with $q = 0.11$ Å are in fairly good agreement with the observed values listed in the last column of the tables. Similarly, for crotonaldehyde the calculated values with $q = 0.115$ Å are in reasonably good agreement with the observation.

Table I. Relative intensities of the C=O progression band in acrolein

Band	q = 0.10 Å	q = 0.11 Å	q = 0.12 Å	Obsd. intensity
0—0	1.00	1.00	1.00	1.00
0—1	1.81	1.99	2.60	1.48
0—2	1.90	2.27	3.76	2.07
0—3	1.50	1.93	3.94	2.20
0—4	0.99	1.36	3.40	1.95

Table II. Relative intensities of the C=O progression bands in crotonaldehyde

Band	q = 0.11 Å	q = 0.115 Å	q = 0.12 Å	Obsd. intensity
0—0	1.00	1.00	1.00	1.00
0—1	2.17	2.37	2.62	2.00
0—2	2.74	3.23	3.83	3.04
0—3	2.59	3.28	4.10	3.63
0—4	2.04	2.74	3.65	3.35

On the other hand, an empirical relation between the C=O bond length and its vibrational frequency has been given by Layton et al.[10]. From using this empirical relation the q values were estimated, and were compared with our calculated q values given in Table III. The agreement is quite satisfactory. From the above results we may conclude that the C=O bond distances of acrolein and crotonaldehyde increase by about 0.1 Å during n-π^* transition. In this calculation q values may be correct within 0.01 Å.

Table III.

	Acrolein	Crotonaldehyde
q(Layton)	0.11 Å	0.11 Å
q(calc.)	0.11 Å	0.115 Å

10) E. M. Layton, J. R. D. Kross and V. A. Fassel, *J. Chem. Phys.*, **25**, 135 (1956).

Summary

The positions vibrational structures and blue-shifts of absorption spectra of acrolein and crotonaldehyde in 33300～25000 cm^{-1} region suggest that the transition is of the n-π^* type. They are similar in vibrational structure except that the crotonaldehyde absorption is shifted towards higher frequencies with respect to that of acrolein. The vapor frequency of the 0–0 band is 25873 cm^{-1} for acrolein, smaller by 654 cm^{-1} than that of crotonaldehyde. The acrolein absorption has 1427, 1271 and 498 cm^{-1} progressions, which are assigned to the C=C stretching frequency, the C=O stretching frequency and skeletal bending frequency in the excited state, respectively. For the crotonaldehyde there are 1360, 1237 and 450 cm^{-1} progressions, which are assigned to the C=C stretching frequency, the C=O stretching and the skeletal bending vibration in the excited state, respectively According to our calculation, the elongation q in the carbonyl bond length during the n-π^* transition, is estimated to be approximately 0.1 Å.

The auther wishes to express his sincere thanks to Professor S. Imanishi and Dr. Y. Kanda for their encouragement throughout this work. He is also indebted to Dr. M. Ito and Mr. A. Sadō for their helpful advice and discussions.

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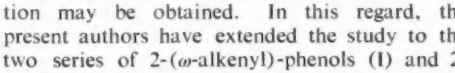
Intramolecular Interaction between Hydroxyl Group and π-Electrons. VII[1]. *Limitation of the Interaction by Chain Length in 2-(ω-Alkenyl)-phenols and 2-(ω-Phenylalkyl)-phenols*

By Michinori Ōki and Hiizu Iwamura

(Received November 16, 1959)

In the previous papers of this series[1,2,3], the authors treated the limitation of the intramolecular interaction between the alcoholic hydroxyl group and π-electrons by the chain length in ω-hydroxy-1-alkenes and ω-phenylalkanols and it has been found that, in the former series, the interaction is observed up to 3-buten-1-ol and in the latter up to 2-phenylethanol[4]. The shift of wave numbers of the O–H stretching vibration (ν_{O-H}) from the free ν_{O-H} to the interacting one, and the absolute intensities of these bands in the infrared absorption were discussed with respect to the configuration, the energy and the entropy of the interaction.

As the phenolic hydroxyl group has a stronger proton donating power in the hydrogen bonding than the alcoholic one, it is naturally expected that the replacement of the alcoholic hydroxyl group in the compounds already studied by the phenolic one will release the limitation of the interaction to compounds with chains longer by one or more carbon atoms and thus some elucidation of the nature of the interaction may be obtained. In this regard, the present authors have extended the study to the two series of 2-(ω-alkenyl)-phenols (I) and 2-(ω-phenylalkyl)-phenols (II), thus completing all the types of the interaction between the alcoholic and phenolic hydroxyl groups and olefinic and benzenoid π-electrons.



I II

It has been reported that 2-allylphenol, a compound of series I, shows two ν_{O-H} maxima in the 3 μ region of the infrared absorption spectra[2]. The data for 2-hydroxybiphenyl, the lowest member of the second series II, are also available[6]. These two compounds were reexamined together with others, a high precision grating infrared spectrometer[2] being used.

Experimental

Measurement and Calculation.—They were performed similarly as described previously[2]. For the decision of the disappearance of the weaker bands, the measurements were carried out with a quartz cell of 5 cm. optical length without alteration in concentration, which enables to detect a very weak absorption, even if the extinction coefficients were as small as one.

Materials.—The phenols used for the measurement are all known, except 2-(3-butenyl)-phenol, and were prepared in the following ways. The physical constants, after fractional distillation under diminished pressure, well agreed with those in the literature.

2-Vinylphenol (I, n=0).—*o*-Coumaric acid was decarboxylated by heating under diminished pressure (ca. 20 mmHg)[7]. B. p. 112°C/17 mmHg, n_D^{27} 1.5775 (lit.[7], b. p. 93~94°C/12 mmHg, $n_D^{25.7}$ 1.577).

2-Allylphenol (I, n=1).—Allyl phenyl ether was submitted to Claisen rearrangement[8]. B. p. 109°C/23 mmHg, n_D^{21} 1.5451 (lit[8]., 99°C/12 mmHg, n_D^{20} 1.5453).

2-(3-Butenyl)-phenol (I, n=2).—A Grignard reagent was prepared from 31.3 g. (0.2 mol.) of *o*-methoxybenzyl chloride[9], 6 g. (0.25 atom) of magnesium and 150 ml. of ether and the supernatant solution was decanted into a dry flask. To the Grignard solution 24.2 g. (0.2 mol.) of allyl bromide in 50 ml. of ether was added and the mixture was refluxed for two hours to complete the reaction. The mixture was decomposed with aqueous ammonium chloride and the ether layer was dried over potassium carbonate. Fractional distillation gave 19 g. (59% of the theoretical) of 4-(2-methoxyphenyl)-1-butene, b. p. 120~123°C/18 mmHg. To a solution of methylmagnesium iodide prepared from 71 g. (0.5 mol.) of methyl iodide, 12.2 g. (0.5 atom) of magnesium and 200 ml. of ether was added 19 g. of 4-(2-methoxyphenyl)-1-butene. Ether was evaporated and the temperature was gradually raised up to 160° on an oil bath. During this time the mixture became pasty and evolution of ethane was observed. Heating was continued for two hours,

1) Part VI: M. Ōki and H. Iwamura, This Bulletin, **32**, 1135 (1959).
2) Part II: idem, ibid., **32**, 567 (1959).
3) Part V: idem, ibid., **32**, 955 (1959).
4) In γ-arylpropanols with such electron donating ring substituents as amino, methoxyl and methyl groups, the interaction was found to be operative, but in γ-phenylpropanol itself it was indecisive.
5) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958); R. West, ibid., **81**, 1614 (1959).
6) O. R. Wulf, ibid., 58, 2290 (1936); V. von Keussler and G. Rossmy, *Z. Elektrochem.*, **60**, 136 (1956).
7) K. Fries and G. Fickewirth, *Ber.*, **41**, 367 (1908).
8) D. S. Tarbell, Org. Reactions, Vol. II, p. 27 (1944), John Wiley & Sons, New York.
9) M. Simonetta and G. Favini, *J. Chem. Soc.*, 1954, 1840.

until the evolution of the gas practically ended. The mixture was dissolved in dilute acetic acid and extracted with ether. The ether extracts were extracted with aqueous sodium hydroxide. The aqueous layer was shaken with ether, treated with Norite, and then acidified with dilute hydrochloric acid. Ether extraction followed by fractional distillation gave 12.5 g. of the desired phenol (72% of the theoretical), b.p., 78°C/2.5 mmHg, n_D^{24} 1.5347. *Anal.* Found: C, 80.67; H, 8.31%. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

2-Hydroxybiphenyl (II, n=0). — A commercial product was recrystallized from petroleum ether (b. p. 50~70°C). M. p., 59.0°C (lit[10]., 59°C).

2-Benzylphenol (II, n=1). — Sodium phenolate was C-benzylated with benzyl chloride in toluene according to the method described by L. Claisen and his co-workers[11]. They obtained dimorph, melting at 21°C and 52°C respectively, while the species used in the present work melted at 21C°.

2-Phenethylphenol (II, n=2). — 2-Hydroxystilbene[12] was quantitatively hydrogenated over Raney Ni catalyst. The substance, after recrystallization from benzene, melts at 81°C (lit.,[13] 81°C).

2-(3-Phenylpropyl)-phenol (II, n=3). — To a Grignard reagent prepared from 37 g. (0.2 mol.) of phenethyl bromide, 4.8 g. (0.2 atom) of magnesium and 100 ml. of ether, was added 9.2 g. (0.075 mol.) of salicylaldehyde in 50 ml. of ether, and the mixture was refluxed for two hours under stirring and then was decomposed with dilute acetic acid. The ether layer was separated, washed with aqueous sodium carbonate and dried over potassium carbonate. After evaporating the solvent, the residue was recrystallized from ligroin, giving 13.5 g. of 2-(1-hydroxy-3-phenylpropyl)-phenol (80% of the theoretical), m. p., 60~61°C. *Anal.* Found; C, 78.85, H, 7.05%. Calcd. for $C_{15}H_{16}O_2$: C, 78.92, H, 7.06%. 2-(1-Hydroxy-3-phenylpropyl)-phenol (12.15 g., 0.053 mol.) and 4 g. of a palladium-on-carbon catalyst (5% Pd) in 50 ml. of ethanol were shaken with hydrogen under atmospheric pressure. In one and half hours 1.34 l. of hydrogen was absorbed and the absorption practically stopped. After removing the catalyst and evaporating the solvent, the residue was distilled under diminished pressure, b. p., 148~150°C/2.5 mmHg. The distillate set to needles and melted at 21°C. The reported melting point is 21°C[14].

Results and Discussion

The apparent O–H stretching absorption curves of the phenols examined are shown in Figs. 1 and 2, and the data of the two bands in each compounds are recorded in Tables I and II.

It should first be noted that in these phenols the free O–H stretching absorption bands at ca. 3610 cm^{-1} are always absolutely symmetric in contrast to the unsymetric ones in the free O–H stretching absorption bands in alcohols. This fact gives a support to the idea of the existence of the rotational isomers in alcohols, tentatively developed in a previous paper[15] on the unsymmetry of the free ν_{O-H} bands of almost all alcohols.

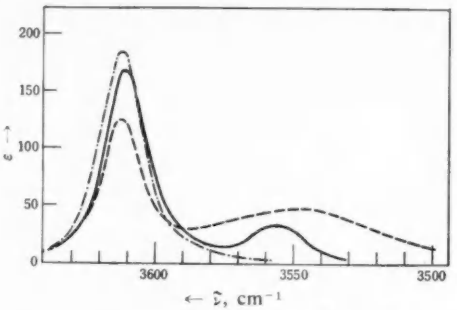


Fig. 1. ν_{O-H} absorptions of 2-(ω-alkenyl)-phenols o-$HOC_6H_4(CH_2)_nCH{=}CH_2$.
$n=0$ ——, $n=1$ – – –, $n=2$ —·—·—.

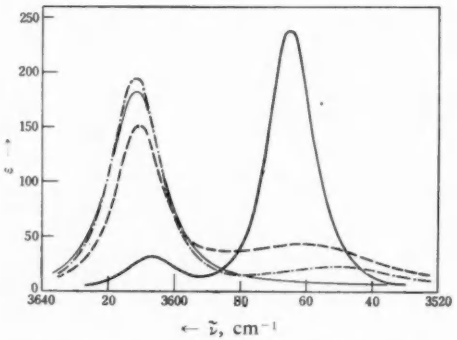


Fig. 2. ν_{O-H} absorptions of 2-(ω-phenylalkyl)-phenols o-$HOC_6H_4(CH_2)_nC_6H_5$.
$n=0$ ——, $n=1$ – – –, $n=2$ —·—·—, $n=3$ ——.

In series I, the interaction is effective up to 2-allylphenol (I, $n=1$); the number of the carbon atoms between the hydroxyl group and the nearest carbon atom which carries the π-electron participating in the interaction is three. It is one more than that in 3-buten-1-ol. In series II, the interaction is discernible up to 2-phenethylphenol (II, $n=2$), the number of the intervening carbon atom being two more than that in 2-phenylethanol. It can, therefore, be said that the limitation by the chain length is released by one or two carbon atoms, when an alcoholic hydroxyl group is replaced by a phenolic one, and the results can be

10) W. Hückel, O. Neunhoeffer, A. Gercke and E. Frank, *Ann.*, **477**, 123 (1930).
11) L. Claisen, F. Kremers F. Roth and E. Tietze, ibid., **442**, 210 (1925).
12) H. P. Kaufmann, ibid., **433**, 237 (1923).
13) St. von Kostanecki, A. Rost and W. Szabranski, *Ber.*, **38**, 743 (1905).
14) A. Greewood and M. Nierenstein, *J. Chem. Soc.*, **1920**, 1595.
15) M. Ōki and H. Iwamura, This Bulletin, **32**, 950 (1959).

TABLE I. ν_{O-H} ABSORPTIONS OF 2-(ω-ALKENYL)-PHENOLS o-$HOC_6H_4(CH_2)_nCH{=}CH_2$

n	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
0	f.	3611.0	17.8	1.08	53.9	0.26
	i.	3556.8	24.4	0.28		
1	f.	3612.5	16.0	0.67	63.7	1.69
	i.	3548.8	67.4	1.13		
2	f.	3612.4	17.9	1.19	—	—

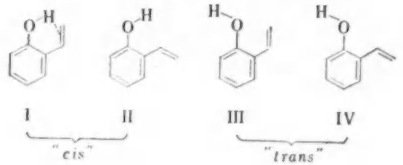
TABLE II. ν_{O-H} ABSORPTIONS OF 2-(ω-PHENYLALKYL)-PHENOLS o-$HOC_6H_4(CH_2)_nC_6H_5$

n	ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^a_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
0	f.	3607.0	18.2	0.20	42.0	6.4
	i.	3565.0	15.0	1.28		
1	f.	3611.0	17.0	0.87	50.9	0.92
	i.	3560.1	56.2	0.80		
2	f.	3612.0	17.0	1.20	61.5	0.29
	i.	3550.5	47.4	0.35		
3	f.	3611.7	19.5	1.28	—	—

attributed to the higher acidity and the favorable structure of the phenols. In alcohols, intervening carbon atoms are all those of methylenes and there are many internal rotational degrees of freedom, of which carbon skeletons must take an *eclipsed* or at least a *gauche* form for the interaction. This is disadvantageous not only to the energy but also to the entropy of the interaction. In phenols, however, at least O–C=C–C bonds are fixed in a *cis* conformation which is favorable for the interaction. These two factors can not be evaluated quantitatively so far as the present data are concerned.

Although it has been established[16] that the shifts in wave numbers in similar classes of compounds correspond to the lengthening of the X–H bond and to the energy of the interaction, it is not yet known whether this pinciple is applicable to the phenomenon the present authors are dealing with. The energy difference in the free and the interacting forms will be dealt with in the following paper. Although the relationship between the energy and the wave number shift is ambiguous, the following will be still valid in this interaction as is empirically known; 1) The intensities represent the number of the molecules with the hydroxyl group related to the appropriate bands and are dependent not only on the energy but also on the entropy factor. 2) The half band-widths correspond to the rotational degree of freedom.

The most appreciable difference between 2-(ω-alkenyl)-phenols and 2-(ω-phenylalkyl)-phenols is found in the lowest members of the series. 2-Hydroxybiphenyl has 6.4 times as many molecules of the interacting form as those of the free, while 2-vinylphenol has the ratio of only 0.2, the free form being predominant provided that the light absorption per molecule is equal in both free and interacting forms. This phenomenon could be explained in the following way. It is generally accepted that the hydroxyl hydrogen in phenol is situated in the plane of the benzene ring so that 2pπ electrons on the oxygen atom can conjugate with π-electrons in the benzene ring, and this gives rise to the so-called "*cis*" and "*trans*" isomerism in ortho-substituted phenols[6,17]. In the biphenyl molecule, the "*trans*" form gives normal free O–H stretching vibration, while "*cis*" can not help taking the interacting form. Differing from this situation, 2-vinylphenol can be regarded as the composite of the following four conformations (I~IV) and the hydroxyl group in the



conformation I only can interact with the π-electrons of the vinyl group. Moreover, a full development of conjugation between the benzene ring and the vinyl group will be favored in the conformations II, III and IV which involve less steric interference. Thus the resonance stabilization favors the predominant contribution of II, III and IV in the equilibrium mixture and this is clearly disadvantageous to the interaction. On the other hand, the biphenyl molecule, except in the solid state, has been known not

16) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); R. Badger and S. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

17) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N. Y., 1945, p. 322.

Table III. ν_{O-H} Absorption of 2-hydroxystilbene

ν_{O-H}	ν_{max} cm^{-1}	$\Delta\nu^{e}_{1/2}$ cm^{-1}	$A\times10^{-4}$ mol^{-1} l. cm^{-2}	$\Delta\nu_{max}$ cm^{-1}	A_i/A_f
f.	3609.0	17.2	1.10	54.8	0.13
i.	3554.2	21.5	0.14		

to exist in the co-planar structure, but in the crossed structure, the angle between the two benzene rings being regarded as large as ca. 50°[18]. This enables the hydrogen atom of the "*cis*" O–H group to come to the very head of the π-electron clouds. In the interacting conformation of the 2-vinylphenol, the plane of the vinyl group is closely co-planar with that of the benzene ring and the hydrogen atom of the hydroxyl group must approach the π-electron clouds from the side. This difference in the angle of hydrogen approach in the interaction must have a significance to the amount of the interaction, and this kind of mechanism will be dealt with in future issues.

The half band-widths of the interacting ν_{O-H} become greater when a methylene chain is introduced between the hydroxyl group and the group carrying the π-electrons. This is without doubt caused by the participation of many rotational sub-levels to the fundamental transition of the O-H stretching vibration. The interacting forms of these molecules are therefore fairly complicated and have an appreciable degree of freedom.

Inspection of the data obtained with 2-benzylphenol and with 2-allylphenol indicates that these compounds give similar absorption for the interacting form. If this is taken as a significant indication, then it would possibly be the π-electron nearest[19] to the hydroxyl group that accepts the proton. However, it is not proved which π-electron interacts with the hydroxyl group. Hence the above mention is only of a reserved significance.

The measurement was extended to 2-hydroxystilbene, which had been proved to be a *trans*-form from the ultraviolet spectrum[12]. The proton acceptor must be the π-electrons on the central ethylene linkage from the structural requirement. The band properties for O–H stretching vibrations are shown in Table III.

The weaker interaction than that in 2-vinylphenol can be explained on the basis of the electronic effect of the phenyl group attached to the vinyl group, that is, the phenyl group diminishes the electron density on the proton acceptor. This presents a striking contrast to the increased interaction in *o*-propenylphenol, in which the methyl group attached to the vinyl group enriches the π-electron densities at the latter[20].

The authors are indebted to Professor Y. Urushibara and Professor T. Shimanouchi for their encouragement and discussion throughout this work. The authors' thanks are also due to the Ministry of Education for the Grant in Aid for Fundamental Scientific Research.

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18) O. Bastiansen, *Acta Chem. Scand.*, 3, 408 (1949).
19) The authors are meaning the π-electron to be another than that born on the phenolic ring.
20) M. Ōki and H. Iwamura, unpublished. See also Reference 5).

Constitution and Solubility of Vitreous Phosphates and Slags

By Jumpei ANDO

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Recently various sorts of fused phosphates and slags are being used as fertilizers to supply lime, magnesia, phosphorus pentoxide, silica and other components necessary for plants. Most of these fused phosphates and slags are produced by quenching the melts with water and thus are almost vitreous containing little crystalline minerals. The constitution of such vitreous substances have not yet been clarified, though many studies have been made on crystalline minerals.

In the present work, the constitution of such vitreous substances was investigated by X-ray diffraction, and thus citrate solubility or acid solubility of those were clarified.

Experimental

Samples.—More than seventy samples including fused phosphates, slags and glasses produced in large scale or pilot plants or in the laboratory were tested by means of X-ray diffraction and microscope. Samples which were almost completely vitreous containing less than 2~3% crystalline minerals were classified according to their chemical composition (Table I).

Samples marked as **CMSP** or **CMASP** are calcium magensium phosphate fused by electric furnaces using phosphate rock and serpentine, or by blast furnaces using phosphate rock, garnierite (nickel magnesium silicate ore) and gypsum to produce nickel matte at the same time[1,2]. Samples marked as **CSP** are slags of phosphorus production by electric furnaces. Samples marked as **CMAFS** are slags of nickel production from garnierite, limestone and gypsum. A sample **CMAS-6** is a blast furnace slag of iron production.

Samples marked as **CP**, **MP**, **CMP** and **NP** were prepared by fusion of mixtures of pure chemicals in platinum crucibles. Other samples were fused in graphite crucibles in the laboratory. Each sample was fused at the temperature 100~200°C higher than the softening point (Table I). Most of these were quenched by water and others were quenched by air.

Among these samples **CMAFS-1,2** contain 2~3% crystalline minerals such as forstelite etc. **CMAS-6** contains 2~3% melilite (Fig. 1). Blast furnace slags containing more lime include more amount of melilite. Other samples are nearly completely vitreous, containing less than 1% crystalline materials.

1) J. Ando, *J. Chem. Soc., Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1134 (1958).
2) J. Ando, *Ind. Eng. Chem.*, **51**, 1267 (1959).

Measurement of Halos by X-ray Diffractometer.—X-ray diffraction patterns of all samples were recorded by X-ray diffractometer under conditions described in Fig. 1. Every sample gave single diffraction maximum (halo) between the diffraction angle of 20~40°. At first when recorded by the voltage of 30kV., each sample gave another maximum around 8~15°, which diminished when the voltage was reduced to 15kV. explaining that this maximum

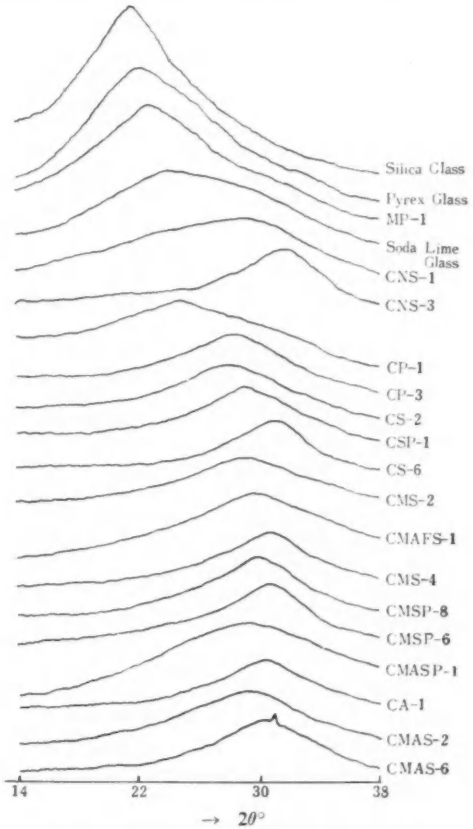

Fig. 1. X-ray diffraction patterns of samples.
Cu ray (15kV., 15 milliamp.), Ni filter
Slit 2.5°, 2.5° and 0.8 mm.
Sample area 16×33 mm.
Time constant 8 sec.
Full scale 400 counts/sec.
Scanning speed 2°/min.
Chart speed 1 cm./min.

TABLE I. CHEMICAL COMPOSITION (%) AND SOFTENING POINT (°C) OF SAMPLES

Mark	SiO_2	Al_2O_3	FeO	MgO	CaO	P_2O_5	S. P.
CP-1	—	—	—	—	28.3	72.3	965
CP-2	—	—	—	—	32.7	68.0	—
CP-3	—	—	—	—	35.8	65.4	1040
MP-1	—	—	—	21.2	—	80.2	1140
MP-2	—	—	—	34.4	—	76.4	1145
CMP-1	—	—	—	14.4	17.0	68.6	990
CMP-2	—	—	—	14.4	23.2	62.2	—
CMP-3	—	—	—	24.7	19.0	56.3	1070
CMSP-1	42.1	0.7	1.4	13.7	25.8	12.6	1275
CMSP-2	40.3	1.8	0.9	15.7	26.0	12.7	1265
CMSP-3	34.0	0.8	0.8	15.7	27.8	19.0	1235
CMSP-4	39.3	0.6	1.4	16.6	26.1	12.0	1260
CMSP-5	39.0	0.6	1.6	15.7	27.4	11.8	1270
CMSP-6	26.0	2.0	1.6	18.7	30.0	19.5	1260
CMSP-7	23.8	1.3	4.1	17.1	31.0	20.6	1270
CMSP-8	21.0	2.1	0.9	10.6	38.9	25.8	1275
CMASP-1	43.0	6.0	6.5	21.7	17.0	5.7	1235
CMASP-2	29.5	7.1	3.1	11.7	30.1	18.5	1215
CMASP-3	38.0	5.3	6.1	16.8	22.9	9.3	1230
CMASP-4	32.7	5.0	6.1	15.3	28.4	13.0	1250
CASP-1	29.1	15.8	0.2	0.3	39.3	15.4	1350
CASP-2	26.5	15.1	0.2	0.4	43.5	13.6	1320
CSP-1	49.3	1.8	0.2	0.3	45.6	2.1	1425
CSP-2	46.8	1.4	0.2	0.8	49.6	1.8	1410
CS-1	65.2	0.4	—	—	34.8	—	—
CS-2	61.3	0.4	—	—	38.3	—	1430
CS-3	56.0	0.4	—	—	43.4	—	1460
CS-4	53.7	0.6	—	—	45.9	—	1490
CS-5	48.5	0.5	—	—	50.6	—	1475
CS-6	46.0	0.3	—	—	53.9	—	1440
CS-7	44.3	0.7	—	—	55.0	—	1425
CMS-1	57.8	1.0	1.2	14.0	26.0	—	—
CMS-2	55.5	0.9	0.5	12.8	29.8	—	1330
CMS-3	51.3	0.9	0.6	15.7	31.2	—	1330
CMS-4	44.6	0.6	1.0	18.8	31.9	—	1315
CMS-5	44.3	1.6	1.0	17.4	35.0	—	1380
CMAFS-1	44.7	6.6	6.6	18.0	23.6	—	1270
CMAFS-2	45.5	5.8	6.3	17.8	25.3	—	1285
CA-1	5.6	53.1	2.4	0.1	37.2	—	1420
CA-2	5.3	50.1	2.0	0.1	40.7	—	1340
CA-3	5.0	48.0	1.8	3.8	39.9	—	—
CA-4	5.8	45.2	1.5	0.2	46.2	—	1385
CAS-1	44.9	19.9	0.5	0.2	32.9	—	—
CAS-2	42.0	20.1	0.7	0.3	35.8	—	—
CAS-3	38.7	19.9	0.4	0.3	39.3	—	1270
CAS-4	36.3	20.0	0.3	0.3	41.7	—	1290
CMAS-1	45.7	13.4	0.5	6.1	32.3	—	1180
CMAS-2	42.0	14.1	0.7	6.4	34.3	—	1200
CMAS-3	38.9	15.0	0.5	6.8	36.3	—	1220
CMAS-4	35.3	15.8	0.7	7.2	38.3	—	1320
CMAS-5	32.5	15.9	1.3	9.4	38.6	—	1340
CMAS-6	32.1	16.5	0.7	7.5	40.2	—	1350
NP-1	—	(Na_2O	30.4)	—	—	69.6	—
NP-2	—	(Na_2O	36.2)	—	—	63.8	—
CNS-1	67.0	(Na_2O	17.3)	—	15.7	—	—
CNS-2	51.0	(Na_2O	25.8)	—	23.2	—	—
CNS-3	46.0	(Na_2O	33.3)	—	20.7	—	—

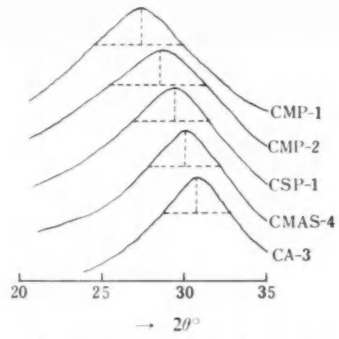

Fig. 2. Precise recording of X-ray halos and measurement of the angle of center of halos.
Cu ray (15kV. 15 milliamp.), Ni filter
Slit 2.5°, 2.5° and 0.8 mm.
Sample area 16×33 mm.
Time constant 16 sec.
Full scale 250 counts/sec.
Scanning speed 0.5°/min.
Chart speed 0.25 cm./min.

was caused by white X-ray which was not cut satisfactorily by nickel filter.

As an interesting relationship of halos to the composition of glasses was found, the halos were recorded more precisely as is illustrated in Fig. 2 in order to measure the angle of the center of halos. The diffraction angles of the center and of maximum of each halo coincide approximately but not exactly.

Measurement of Solubility.—All samples were crushed so as to have the following grain sizes: 60~100 mesh 10%, 100~200 mesh 40%, and under 200 mesh 50%. To 1 g. sample 150 ml. of 2% citric acid or N/2 (about 1.8%) hydrochloric acid was added, shaken for 5, 15, 30 or 60 min. at 20 or 30 °C, then filtered quickly using suction. The insoluble residue was dried and weighed. In this case, "Solubility" means the weight loss % measured by such method. "Solubility" when dissolved in a definite time concerns mainly the velocity of dissolution in the case of most vitreous phosphates and slags of basic composition which are dissolved completely by acids ultimately. In such case the solubility of all components of samples, lime, magnesia, alumina, silica, ferrous oxide and phosphorus pentoxide ect., are nearly the same as each other, coinciding with the solubility measured by weight loss of samples.

Some of vitreous samples containing much silica or phosphorus pentoxide are not dissolved by acids completely even when shaken for a long time but leave insoluble residue consisting mainly of a silicic or phosphoric acid component. In such cases solubility of each component was measured by chemical and X-ray analysis of the residue. Citrate solubility (at 65°C) of samples was measured similarly.

Measurement of Softening Point.—Samples were shaped into segel cones of 3 cm. height, fixed on chromite holders, and were heated at a rate of 5°C/min. Temperatures at which the cones fell were measured by platinum-platinum · rhodium thermocouple (Table I).

Results

Relationship of X-ray Diffraction Halos to Chemical Composition, Construction and Properties of Glasses.—*Outline.*—It was found that acidic samples such as silica glass, Pyrex glasses, MP-1 or MP-2 revealed a steep maximum of X-ray diffraction pattern at smaller diffraction angle of 22~24° (Fig. 1). The diffraction maximum (halo) shifts to larger angle according to the increase of the basicity of samples. Each of the samples of moderate basicity, CP-1, 2, CMP-1, soda lime glass, etc., reveals a gentle maximum around 25~29°. These samples of moderate basity have a lower softening point and are renderd to glass state most easily.

Every basic sample such as CMSP-5~8, CS-5~7, CA-4, CMAS-4~6, or CNS-3 reveals at larger angle of 30~32° a halo smaller than that of acidic samples but steeper than that of samples of intermediate basicity. The melts of these samples crystallize very quickly, and therefore can not be rendered to complete glass state without quenching. Samples which were more

TABLE II. RATIOS AND THEIR MEANINGS

$CR = \dfrac{Ca+Na+(1-a)Al+(1-b)Mg+(1-c)Fe-0.1P}{1.1P+Si+aAl+bMg+cFe}$	A ratio of the number of cations which are coordinated by six or eight oxygen ions to that coordinated by four oxygen ions.
$OR_0 = \dfrac{O}{1.1P+Si+aAl+bMg+cFe}$	A ratio of the number of total oxygen ions to that of cations coordinated by four oxygen ions.
$OR_1 = \dfrac{O}{P+Si+aAl}$	A ratio of the number of oxygen ions to that of cations the bond strength of which with oxygen is larger than 80 kcal. (Table IV).
$OR_2 = \dfrac{O}{1.05P+Si+(a+0.05)Al+0.5bMg}$	A part of intermediate cations was added to denominator of OR_1 (Table IV).
$OR_3 = \dfrac{O}{1.08P+Si+(a+0.15)Al+0.8bMg}$	Most of intermediate cations was added to denominator of OR_1.

TABLE III. EXAMPLES OF CALCULATION OF RATIOS

Samples	A.B.N.	a	b	c	CR	OR_1	OR_2	OR_3
CMP-1	—	—	0.30	—	0.40	3.17	2.90	2.76
CASP-1	44	0.50	0.08	0.05	0.96	3.14	3.05	2.92
CMAFS-2	49	0.60	0.10	0.07	1.09	3.18	3.09	3.00
CMAS-1	42	0.43	0.06	0.05	0.98	3.02	2.96	2.87
CMAS-6	52	0.71	0.12	0.07	1.23	3.23	3.12	2.97
CA-2	55	0.73	—	0.08	1.28	3.00	2.80	2.55

TABLE IV. CALCULATED BOND STRENGTH OF OXIDE COMPONENTS

M	Valence	Dissociation energy per MO_x, kcal.	Coordination number	Single bond strength B_{M-O}, kcal.	
Si	4	424	4	119	Glass formers
Al	4	402–317	4	107–79	Glass formers
P	5	442	4	111–88	Glass formers
Al	3	317–402	6	53–67	Intermediates
Mg	2	222	4	56	Intermediates
Ca	2	257	4	66	Intermediates
Mg	2	222	6	37	Glass modifiers
Ca	2	257	6	43	Glass modifiers
Na	1	120	6	20	Glass modifiers
Ca	2	257	8	32	Glass modifiers

basic could not be rendered to complete glass even by rapid quenching with water.

The author thinks that halos of these glasses and vitreous substances are chiefly determined by the ratio of the number of cations coordinated by six (or eight) oxygen ions to that coordinated by four oxygen ions. This ratio is shown as "coordination ratio" (CR) in Table II and Fig. 3. X-ray is chiefly diffracted to smaller angle by oxide glasses containing much SiO_4, PO_4, MgO_4 etc. because these tetrahedra are apt to form hexagonal rings or chains having larger spacing. On the contrary, CaO_6, MgO_6, NaO_6 etc. are apt to form tetragonal rings having smaller spacing, and thus diffract X ray to larger angle. When nearly equal amount of RO_4 and RO_6 is mixed the gentle halo appears in intermediate angle.

The strongest diffraction peaks of the more basic crystalline minerals of each CaO-P_2O_5, CaO-SiO_2, CaO-Al_2O_3, CaO-Al_2O_3-SiO_2 or other systems appear usually at larger angle: e. g. $CP \rightarrow C_2P \rightarrow C_3P$, $S \rightarrow CS \rightarrow C_2S$, $C_3A_5 \rightarrow CA \rightarrow C_3A$, $CAS_2 \rightarrow C_2AS$, etc. Moreover, the diffraction angle of the strongest peak of CP (calcium metaphosphate) coincides with that of the center of the halo of the glass of the same chemical composition similarly as in the case of cristobalite and silica glass. These facts show that there is some relation between the structure of glass and that of crystalline mineral. However, the diffraction peaks of crystalline minerals and halos of glasses of the same composition do not always agree with each other.

Empirical formula indicating the relation of X-ray halo to chemical composition and constitution of glasses.—It was found that for every glasses consisting of silica, alumina, lime, phosphorus pentoxide, magnesia, sodium oxide and ferrous oxide there was simple relation between the diffraction angle (or $\lambda/\sin\theta$) of the center of each halo and the value of the above-mentioned coordination ratio (Table II, Fig. 3).

In the ratio Ca, Mg, Al, Si, etc. are the number of each ion (or atom) in a unit volume of glasses. Coefficients a, b and c are given by

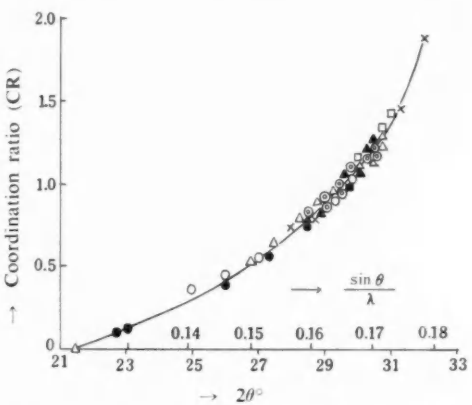

Fig. 3. Relationship of the diffraction angle or $\sin\theta/\lambda$ of center of halo to coordination ratio.
○ CP, CASP ▲ CMS, CMAFS
◎ CMSP, CMASP □ CA, CAS
● MP, CMP ■ CMAS
△ CS, CSP × NP, CNS

Fig. 4 which illustrates the relationship of the coefficients to apparent basicity number A. B. N. ($= CaO + MgO + 0.7FeO + 0.25Al_2O_3$). Here, CaO, MgO, FeO and Al_2O_3 of A. B. N. are weight % of each component of glasses. Fig. 4 was plotted empirically by trial-and-error method in consideration of both X-ray halo and solubility of glasses which will be described below. The coefficients a, b or c indicates principally a ratio of numbers of aluminum, magnesium and iron ions which are coordinated by four oxygen ions [these are described as Al(4), Mg(4) and Fe(4) below] to that of total aluminum, magnesium or iron ions respectively.

The apparent basicity number (A. B. N.) of calcium magnesium phosphate, slags of iron, nickel or phosphorus production which are being used as fertilizers is usually 47~52, and therefore, a=0.6~0.7, b=0.10~0.12, and c=0.06~0.07. In the case of aluminous glass containing much alumina the change of the coefficient a is smaller than in the case of glasses containing less alumina (Fig. 4).

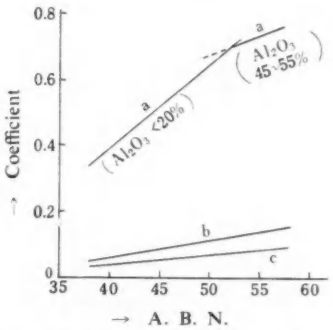

Fig. 4. Relationship of A. B. N. to the coefficients.

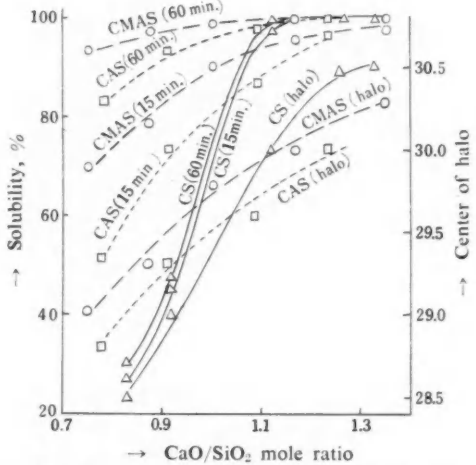

Fig. 5. Relationship of CaO/SiO_2 mole ratio to the solubility in N/2 hydrochloric acid (60 min. at 30°C) and to the angle of the center of halo.

As is illustrated by Fig. 5 both the diffraction angle of the center of each halo and hydrochloric acid solubility of samples of CS(CaO-SiO_2) system are reduced remarkably according to the decrease of CaO/SiO_2 mole ratio. However, the reduction of both the angle and the solubility is far smaller for the samples containing a considerable amount of alumina or magnesia and alumina (samples of CAS or CMAS systems). This is attributable to the change of oxygen coordination number of aluminum and magnesium ions—much Al(4), Mg(4) and less Al(6), Mg(6) occur in basic glasses, less Al(4), Mg(4) and much Al(6), Mg(6) occur in acidic glasses as is illustrated by Fig. 4.

It was found by both X-ray and solubility tests that in glasses which contain phosphorus pentoxide more Mg(4), Al(4) and Fe(4) occurred than in silicate glasses. The amount of such four coordinated ions increases according to the amount of phosphorus pentoxide. It seems that even a part of calcium or sodium is coordinated by four oxygen ions in phosphate glasses. From this standpoint of view, coefficients of phosphorus 1.1 for denominator and −0.1 for numerator were introduced into coordination ratio (Table II) for convenience of calculation of the value of the ratio. In this way X-ray, patterns and solubilities of phosphate glasses are indicated well (Figs. 3 and 9—11).

Especilly in the case of glasses containing magnesia and much phosphorus pentoxide, an extensive amount of magnesium ions seems to be coordinated by four oxygen ions. The X-ray diffraction halos of silica glass and that of MP-1 which consists of nearly equal mole of magnesia and phosphorus pentoxide resemble each other explaining that MgP_2 plays a role of Si_2. Coefficient b to be used for calculation of coordination ratio of glasses containing more than 40% phosphorus pentoxide is given by Fig.

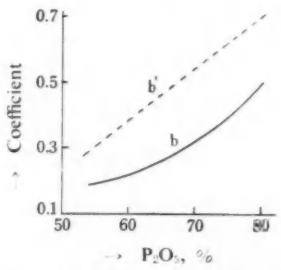

Fig. 6. Relationship of P_2O_5 content to coefficients.

6. In the case of phosphate glass the coefficient a, b or c does not indicate the ratio of the number of Al(4), Mg(4) or Fe(4) to that of total Al, Mg or Fe respectively because coefficients of phosphorus 1.1 and −0.1 are used for conveniene. The approximate ratio of the number of Mg(4) to total Mg of samples of CMP and MP systems is shown by dotted curve (b′) in Fig. 6.

Relationship of glass formation to oxygen ratio.—Oxygen ratio, a ratio of the number of total oxygen ions to that of network-forming ions, is known to relate deeply to glass formation. It was clarified by the present study that approximate oxygen ratio was calculated by ORo (Table II). Samples with the ratio less than 3.0 could easily be rendered to glass without quenching, because these are composed of long chains or networks of oxygen and network-forming ions and the melts of these are viscous. Samples with the ratio 3.0~3.3 could be rendered to glass state completely by water quenching (CMSP-6~8, CS-6, 7, CMS-4, 5, CA-2, 3, CMAS-5, 6, etc.). As an exception high temperature modification of calcium metasilicate (pseude wollastonite) was crystallized very quickly from the melt of the composition $CaO \cdot SiO_2$, oxygen ratio of which is 3.0. This mineral is composed of small Si_3O_9 rings[3] and therefore, is completely soluble in N/2 (about 1.8%) hydrochloric acid, though silicic acid component of the glass of the same composition is not dissolved by the acid.[4] Samples with the ratio larger than 3.3 could not be rendered to complete glass state even by rapid water quenching from high temperature forming crystalline minerals partly. The glass formation is affected by bond strength, too (Table IV).

Solubility of Glasses.—*Relationship of bond strength to citric and hydrochloric solubility.*—In Table IV single bond strength between oxygen and various cations[5] is illustrated. Mg(4), Ca(4) and Ca(6) were inserted by the present author into the table. Iron is thought to be intermediate between calcium and magnesium.

It was clarified in the present study that linkage Si-O, P-O or Al(4)-O, the bond strength of which is more than 80 kcal., could scarcely be broken by 2% citric acid or N/2 hydrochloric acid. The linkage Ca(6)-O, Ca(8)-O, Mg(6)-O, or Na-O, the bond strength of which is less than 50 kcal., is broken by the acids quickly. The linkage of intermediate bond strength such as Al(6)-O, Mg(4)-O, or Ca(4)-O is slowly broken by the acids.

Basic glasses containing less intermediate components are dissolved in acids very quickly

3) J. W. Gruner, *Am. Mineral.*, **33**, 681 (1948).
4) J. Ando and S. Matsuno, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 1481 (1959).
5) Kuan-Han Sun, *J. Am. Ceram. Soc.*, **30**, 277 (1947).

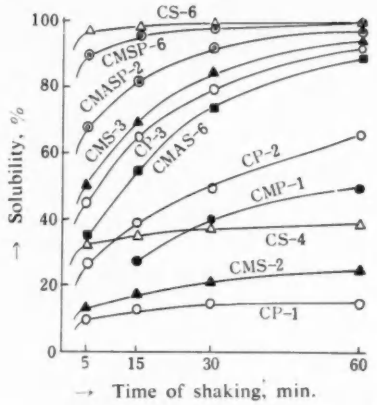

Fig. 7. Citric solubility of samples in various times at 20°C

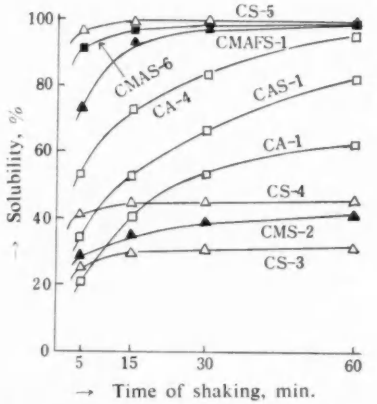

Fig. 8. Solubility of samples in N/2 HCl at 30°C.

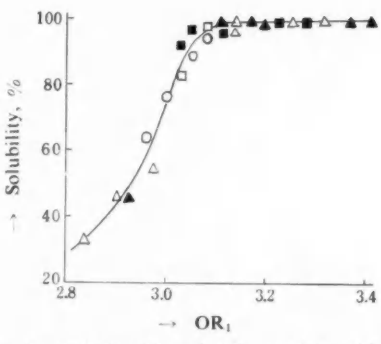

Fig. 9. Relationship of OR_1 to hydrochloric solubility in 60 min. at 30°C.
△ CS, CSP ■ CMAS
▲ CMS, CMAFS ○ CA
□ CAS

(CS-6, CMSP-6 in Fig. 7, CS-5 in Fig. 8., etc.). Basic glasses containing much intermediate components dissolve slowly but completely (CMASP-2, CMS-3, CP-3, CMAS-6, CMAFS-1, CA-4, CAS-3, 4, etc.).

Acidic glasses (CP-1, CS-2, 3, 4, CMS-2, etc.) are not dissolved completely by acids but leave mainly hydrated silica or phosphoric acid component undissolved, because such glasses contain large linkage of P-O-P-O or Si-O-Si-O which forms long chains, large rings or networks. Such large linkages, the bond strength in which is larger than 80 kcal., must not be dissolved into liquid but remain as insoluble residue or as colloidal state. On the contrary, small chains or rings must enter into solution by hydration. The magnitude of the linkage is related to oxygen ratio as will be described below.

Fig. 9 illustrates the relationship of OR_1 (Table II) to the solubility of glasses when shaken in N/2 HCl for an hour at 30°C. Samples with OR_1 larger than 3.2 are dissolved completely. Samples with OR_1 smaller than 3.15 leave insoluble residue. OR_1 3.2~3.15 corresponds to M_5O_{16}~M_6O_{19} which is the linkage of five ~six MO_4 groups and is 10~15 Å in length. It was clarified that the linkages (the bond strength in which is larger than 80 kcal.) smaller than 10 Å entered into solution and that linkages larger than 20 Å did not enter into solution usually but remained undissolved or as colloidal residue.

In citric acid the samples dissolve more slowly than in N/2 HCl. Especially the samples containing much Ca(4), Mg(4) or Al(6) are dissolved slowly and therefore not completely in an hour in 2% citric acid. It was clarified that

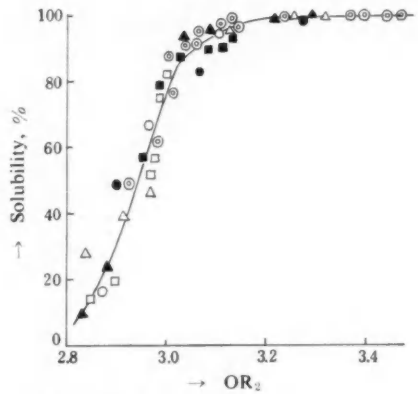

Fig. 10. Relationship of OR_2 to citric solubility in 60 min. at 20°C.

○ CP, CASP ▲ CMS, CMAFS
◎ CMSP, CMASP □ CAS, CA
● CMP ■ CMAS
△ CS, CSP

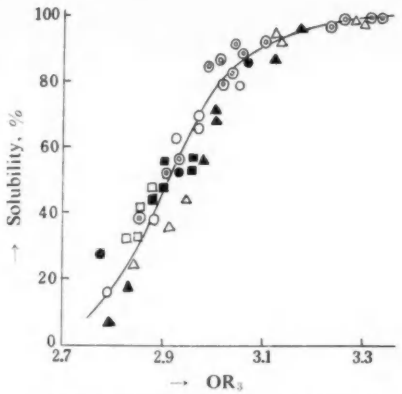

Fig. 11. Relationship OR_3 to citric solubility in 15 min. at 20°C.

○ CP, CASP △ CS, CSP
◎ CMSP, CMASP □ CAS
● CMP ■ CMAS
▲ CMS, CMAFS

citric solubility of samples in 60 or 15 min. at 20°C can be indicated by OR_2 or OR_3 (Table II) as is illustrated by Fig. 10 or 11.

Citric solubility of −200 mesh/inch samples is nearly equal to hydrochloric solubility of −60 mesh/inch samples treated in the same time. Hydrochloric solubility in 15 min. is nearly equal to citric solubility in 60 min. By raising the temperature from 20 to 30°C velocity of dissolution increases somewhat. Thus acid solubility of various vitreous phosphates and slags can be known from chemical composition using above relations.

Citrate solubility. — Citrate solubility by American official method and citric or hydrochloric solubility is quite different. For examble, CP-1 is dissolved very quickly in neutral citrate

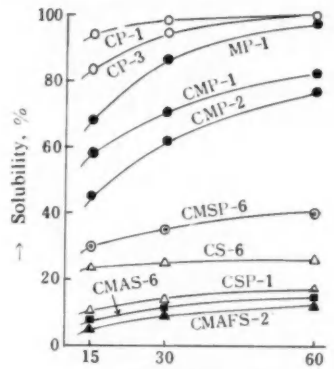

Fig. 12. Citrate solubility of samples in various times at 65°C.

though largely insoluble in acids. Phosphate glasses (CP-1—3, CMP-1—3) are dissolved more quickly in citrate but more slowly in acids when the samples are more acidic containing more phosphorus pentoxide component (Fig. 12). NH_4^+ and OH^- of the citrate must break linkages of P-O-P-O.

Silicate or aluminate glasses is dissolved slightly. Calcium magnesium phosphate, a silicophosphate glass, is dissolved intermediately in citrate (Fig. 12).

Discussion

The relation illustrated in Fig. 3 applies nearly exactly to glasses composed mainly of oxides of sodium, magnesium, aluminum, silicon, phosphorus, potassium and calcium atomic number of which is between 11 and 20. For glasses containing much boron, lithium, lead, barium etc., the atomic number of which is far smaller or far larger than that of the above elements, the relation between X-ray halo and composition of glasses is not so simple. In such cases the X-ray halo must be affected not only by coordination number of cations but also fairly intensely by ionic radius, the number of electron etc.

The above explanations of X-ray halos which was based only on coordination number and especially relations illustrated by Figs. 4 and 6 are not quite exact. However, many facts shown in the present study must be useful to clarify the construction and properties of various glasses and vitreous substances. Moreover, it is possible to determine the chemical composition of glasses by the measurement of X-ray halo.

Quenched phosphates and slags often contain small amount of crystalline minerals which affect the solubility considerably. Usually crystalline minerals dissolve far more slowly than glasses of the same composition. Crystallized forstelite, enstatite, diopside, apatite, anorthite and calcium pyrophosphate scarcely dissolve in citric acid or citrate. Gehlenite dissolves slowly, akermanite and β-tricalcium phosphate dissolve fairly quickly in acids.[6,7] α-Calcium metasilicate[4] and α-tricalcium phosphate dissolve quickly in acids. In citrate α modification of tricalcium phosphate is highly soluble but β modification is less soluble because of the difference of velocity of dissolution which is due to the difference of structure.

Summary

The diffraction angle of center of X-ray halo of glasses composed of silica, phosphorus pentoxide, alumina, lime, magnesia, sodium oxide and ferrous oxide is principally determined by a ratio of the number of cations coordinated by six (or eight) oxygen ions to that coordinated by for oxygen ions.

Approximate ratio of the number of aluminum or magnesium ions which is coordinated by four oxygen ions to that of total aluminum or magnesium ions can be determined by measurement of X-ray halo using above relations.

Glass formation is closely related to oxygen ratio OR_0. Solubility of vitreous phosphates and slags in N/2 hydrochloric acid or 2% citric acid is indicated by the ratios OR_1, OR_2 and OR_3 all of which are calculated from chemical composition and above relations.

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Ternary Liquid Equilibria in System n-Heptane-Thiophene-Liquid Ammonia. New Tie Line Correlation

By Kiyoharu ISHIDA

(Received October 19, 1959)

The removal of organic sulfur compounds from petroleum products has been one of the most important problems in the petroleum refinery field for many years, although the success of the hydro-refining process has reduced the difficulties of the desulfurization. It has been reported that there is a possibility of the use of liquid ammonia and its mixed solvents as desulfurizing agents on the extraction process[1], but no fundamental data in connection with this matter have been given. This paper presents the equilibrium data at temperatures of 20 and 0°C for the system *n*-heptane-thiophene-liquid ammonia, and a new method correlating tie line data for ternary liquid equilibria has been described.

The method used to obtain data for the construction of phase equilibria was the same analytical method as described in the previous paper[2]. The heterogeneous liquid layers were separated and analyzed after the saturation equilibrium was attained in a constant temperature bath regulated within the range of ±0.05°C throughout the experiment. An aliquot of each layer, which was determined from the difference of weight of the bottle containing the system, was released to the receiver and the ammonia was absorbed by the definite quantity of the 2 N sulfuric acid solution after it was removed from the receiver by volatilization, and then backtitrated with 0.5 N standard hydroxide solution. The compositions of ammonia-free organic liquid were determined by measuring their densities and refractive indices to the nearest 0.0001 unit. The results were adjusted for the slight loss of organic liquid by volatilization by means of the lever rule[3] from the composition of the total mixture and the concentrations of ammonia in both layers. It was observed that when the vaporization loss of binary mixtures of heptane and thiophene was less than about 15%, the compositions of organic binary mixtures were practically unaffected with the vaporization of organic liquid accompanied by the determination of ammonia, though the vapor pressure of thiophene has about twice that of *n*-heptane in the neighborhood of 0°C.

n-Heptane used in this investigation was the reference fuel for octane number determination, having the following physical constants, b.p., 98.3°C; d_4^{20}, 0.6838; n_D^{20}, 1.3878. Commercially available thiophene was dissolved in liquid ammonia, allowed to stand overnight, and then redistilled after the yellowish precipitates were removed; the middle fractions having the constants b. p. 84.1°C, d_4^{20} 1.0638, n_D^{20} 1.5288 were used.

Results and Discussion

The data of densities and refractive indices for the binary system of *n*-heptane and thiophene from which the compositions of the raffinate and the extract were determined are given in Table I, and the equilibrium data for the ternary system are given in Table II and shown in Figs. 1 and 2. As will be clear from the figures, tie lines are almost parallel to the base of the triangle and in the case of equilibrium at 0°C the distribution ratio changes from more than unity to less than unity as shown in Fig. 2. The maximum selectivity[3] for this system regarding liquid ammonia as a solvent for the separation of thiophene from paraffin are given to be 72.9 and 62.0 wt. % at 0 and 20°C., respectively. The respective maximum concentrations of thiophene in the extract are 89.3 and 78.8 wt.% at 0 and 20°C., then the maximum

TABLE I. DENSITIES AND REFRACTIVE INDICES FOR *n*-HEPTANE-THIOPHENE BINARY SYSTEM

Thiophene wt. %	d_4^{20}	n_D^{20}
0.0	0.6838	1.3878
12.73	0.7154	1.3977
25.89	0.7514	1.4103
31.73	0.7688	1.4164
53.36	0.8414	1.4432
58.37	0.8607	1.4508
62.36	0.8766	1.4565
74.19	0.9285	1.4764
79.82	0.9554	1.4865
85.98	0.9866	1.4988
92.71	1.0229	1.5128
100.0	1.0638	1.5288

1) V. A. Kalichevsky, *Petroleum Refiner*, **30**, No. 4, 111 (1951).
2) K. Ishida, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **56**, 469 (1953).
3) D. F. Othmer and P. E. Tobias, *Ind. Eng. Chem.*, **34**, 690 (1942).

TABLE II. EQUILIBRIUM DATA FOR THE SYSTEM *n*-HEPTANE-THIOPHENE-LIQUID AMMONIA AT 20.0 AND 0.0°C., wt. %

Total mixture		Hydrocarbon layer		Solvent layer	
Thiophene wt. % (Solvent-free basis)	NH_3 wt. %	NH_3 wt. %	Thiophene wt. % (Solvent-free basis)	NH_3 wt. %	Thiophene wt. % (Solvent-free basis
		At 20.0°C			
0.0	—	4.8	0.0	96.9	0.0
12.7	53.2	5.7	5.6	89.4	61.2
25.9	54.1	6.7	11.5	82.9	73.4
44.7	51.7	8.8	22.0	71.3	78.8
42.3	40.1	10.1	26.8	65.6	77.9
53.4	38.9	13.6	36.0	55.0	75.0
50.8	30.6	15.6	40.6	49.4	72.7
58.4	32.6	22.0	49.2	41.2	67.3
60.7	34.8	23.8	51.1	38.8	65.5
Plait point[a)]		30.7	58.1	30.7	58.1
		At 0.0°C			
0.0	—	2.7	0.0	98.2	0.0
8.9	45.5	2.9	4.8	93.2	74.2[b)]
19.3	52.0	3.4	9.4	88.6	82.4[b)]
33.5	50.7	4.1	17.1	81.2	88.0
36.0	33.7	5.3	25.2	73.3	89.3
50.1	34.5	7.4	35.7	63.4	88.8
56.5	32.8	8.8	41.9	56.9	87.5
62.4	30.0	11.4	49.8	49.0	85.0
63.9	30.6	11.9	50.9	48.1	84.6
78.2	42.3	12.9	52.8	46.5	84.1
73.6	32.8	18.2	61.9	38.4	79.8
Plait point[a)]		28.3	72.5	28.3	72.5

a) The plait point was estimated according to Treybal et al.[4)]

b) This value was calculated from the concentration of ammonia in both layers and the composition of the total mixture and the raffinate.

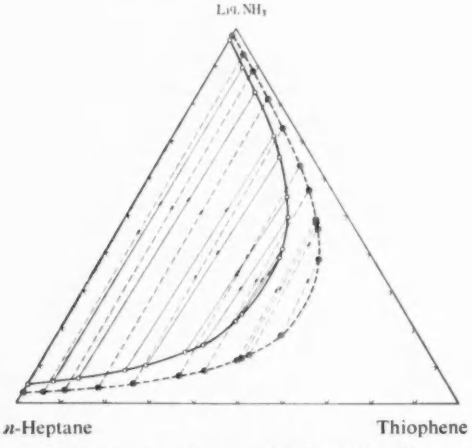

Fig. 1. System *n*-heptane-thiophene-liq. NH_3 at 20 and 0°C, wt. %.

—○— 20.0°C --◎-- 0.0°C

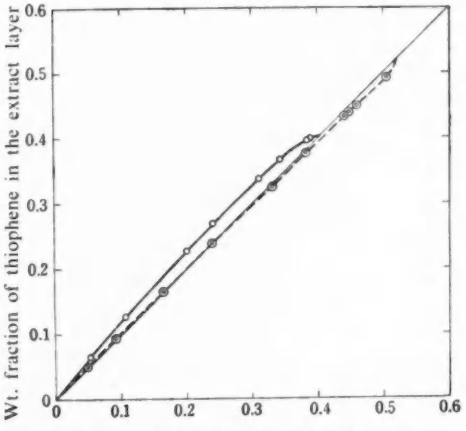

Fig. 2. Equilibrium distribution diagrams for the system *n*-heptane-thiophene-liq. NH_3.

—○— 20.0°C --◎-- 0.0°C

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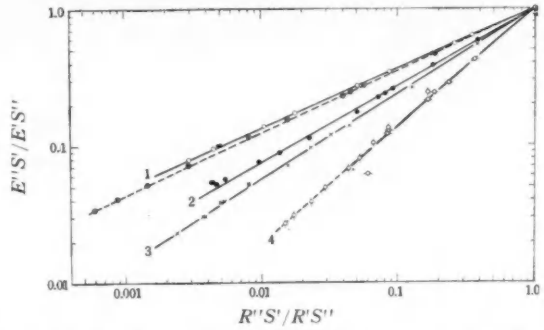

Fig. 3. Plot on logarithmic coordinates $E''S'/E'S''$ against $R''S'/R'S''$ for liquid ammonia systems.

Number	Symbol	System R — E — S	Temperature, °C	Reference
1	—○—	*n*-Heptane—Thiophene—Liq. NH_3	20.0	
	--◎--	*n*-Heptane—Thiophene—Liq. NH_3	0.0	
2	—●—	*n*-Hexane—Benzene—Liq. NH_3	20.0	5)
3	—×—	*n*-Heptane—Toluene—Liq. NH_3	20.0	6)
4	—○—	Ethylbenzene—Styrene—Liq. NH_3	0.0	5)
	--○--	Ethylbenzene—Styrene—Liq. NH_3	−15.5	5)

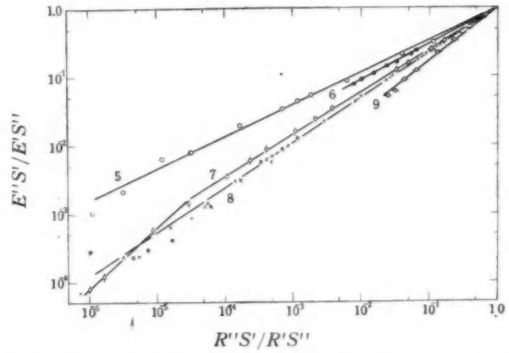

Fig. 4. Plot on logarithmic coordinates of $E''S'/E'S''$ against $R''S'/R'S''$ for systems of various investigators.

Number	Symbol	System R — E — S	Temperature, °C	Reference
5	○	Benzene—Dioxane—Water	25	7)
6	●	Water—Acetic Acid—Furfural	26.7	8)
7	○	Water—Acetic Acid—Toluene	25	9)
8	+	Water—Ethanol—Benzene	25	10)
	×	〃 〃 〃	25	11)
	✳	〃 〃 〃	25	12)
9	-○-	Water—Methanol—Butano	15	13)

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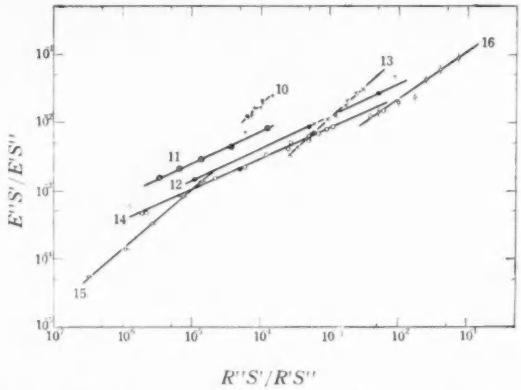

Fig. 5. Plot on logarithmic coordinates of $E''S'/E'S''$ against $R''S'/R'S''$ for systems containing two partially miscible pairs.

Number	Symbol	System R — E — S	Temperature, °C	Reference
10	⊣	*n*-Heptane—Methylcyclohexane—Aniline	25	14)
11	◌	Water—Aetone—Chlorobenzene	25~26	15)
12	●	*n*-Hexane—Methyl ethyl ketone—Water	37.8	16)
13	×	*n*-Heptane—Toluene—Liq. NH_3	−15	6)
14	○	Benzene—Butanol—Water	25	17)
15	-○-	Toluene—Aniline—Water	25	18)
16	◌	Ethyl acetate—*sec*-Butanol—Water	20	19)

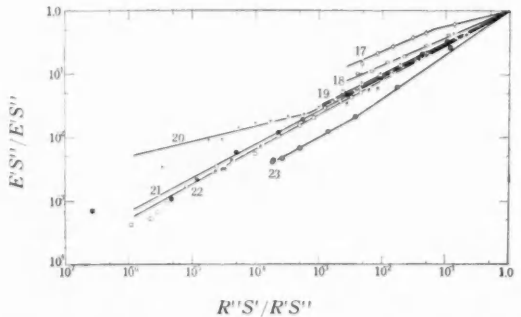

Fig. 6. Plot on logarithmic coordinates of $E''S'/E'S''$ against $R''S'/R'S''$ for solutropic systems.

Number	Symbol	System R — E — S	Temperature, °C	Reference
17	◌	Water—*t*-Butanol—Ethyl acetate	20	19)
18	-○-	Water—Isopropanol—Ethyl acetate	20	19)
19	◌	Water—Acetic acid—Ether	25	20)
20	+, ×, ✳	Water—Pyridine—Benzene	25	21), 22), 23)
21	●	Water—*t*-Butanol—Benzene	25	24)
22	○	Water—Isopropanol—Benzene	25	25)
23	◌	Water—Ethanol—3-Heptanol	25	26)

separation factors[5] become the respective values of 0.650 and 0.488, these values being considerably greater when compared with those in cases of the separation of hydrocarbon mixtures.

Tie Line Correlation

This system as in the other solutropic systems fails to give a straight line having a definite slope from the appropriate plot of conjugate values at equilibrium according to any method which has been proposed by any one of the many investigators as tie line correlations. The author has found that a straight line results from a plot of logarithm of $E''S'/E'S''$ against logarithm of $R''S'/R'S''$ where S, E and R are the respective fractions of the solvent, the solute and the diluent at equilibrium and one prime and two primes denote the diluent-rich layer and the solvent-rich layer, respectively. Plots by this method for the present data are shown in Fig. 3. In Fig. 3, plots for the several systems using liquid ammonia as a solvent are also included. It is observed that these data are correlated by this method satisfactorily.

Several ordinary systems investigated by various workers are plotted in Fig. 4, and plots for systems containing two pairs of partially miscible liquids are given in Fig. 5. Plots by this method for several solutropic systems are shown in Fig. 6. Except for some systems where it seems to be plausible that the data are correlated by two straight lines changing their slopes, the plotted data for most systems fall on straight lines having definite slopes almost within their probable experimental accuracy. When the solvent and the diluent are practically insoluble as in the case of benzene-water binary, values of $S'R''/S''R'$ and $S'E''/S''E'$ become more inaccurate at the lower concentrations of the solute, because the concentrations of the solute are very small and their accurate determinations by ordinary methods are difficult. For this reason, it may be said roughly that plots by this method would give a straight line for most ternary systems.

Since the values of $S'R''/S''R'$ for the binary systems of the diluent and the solvent are located as the abscissa on the left ends of straight lines in these figures, the initial distribution ratio at zero concentration of the solute can be estimated from the ordinate on these points. The ordinate on the right ends of straight lines in Fig. 5 represent the values of $S'E''/S''E'$ for the binary systems of the solute and the solvent, and the abscissa the product of the distribution coefficient at zero concentration of the diluent and the ratio of the concentration of the solvent in the solute rich phase to that in the solvent rich phase.

The straight lines can be represented by equations of the form

$$\log \frac{E''S'}{E'S''} = n \log \frac{R''S'}{R'S''} + k \tag{1}$$

For the ordinary systems which comprise two miscible pairs of liquids and one partially miscible pair, the value of k should be extremely near zero, since the values of $S'E''/S''E'$ and $S'R''/S''R'$ at the plait point are equal to unity. If the relative distribution ratio is designated by β,

$$\beta = \frac{E''}{E'} \cdot \frac{R'}{R''} \tag{2}$$

Then,

$$\log \beta = (n-1) \log \frac{R''S'}{R'S''} + k \tag{3}$$

Therefore, if a plot is made of the relative distribution ratio against the quotient of the ratio of the concentration of the solvent in the diluent rich phase to that in the solvent rich phase and that of the solute or the diluent on the double logarithmic coordinates, a straight line will be given as well not only for ordinary systems, but also for solutropic systems and those containing two partially miscible pairs.

Summary

Phase equilibria for the system *n*-heptane-thiophene-liquid ammonia has been determined at temperatures of 0 and 20°C. A new method has been proposed which correlates tie line data in such a manner that a straight line is obtained for most systems including solutropic systems.

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Polymerization of Methyl Methacrylate Initiated by a Combined Action of p-Tolylsulfonylacetic Acid and Dimethylaniline

By Ryoichi UEHARA

(Received July 20, 1959)

It has been first reported by Lal et al.[1], that the polymerization of methyl methacrylate is initiated by mixtures of dimethylaniline and various carboxylic acids. In a previous paper by the present author[2], results of studies on the kinetics of the polymerization of methyl methacrylate initiated by a combined action of trichloroacetic acid and dimethylaniline have been reported, and a bimolecular reaction between these two compounds has been suggested as the initial reaction of the polymerization. In the report of Lal, per-cent-conversions after 1 hr. in the bulk polymerization of methyl methacrylate at 58.6°C by using nine carboxylic acids have been given briefly, and six acids, i.e., mono-, di- and trichloroacetic, mercaptoacetic, phenoxyacetic and 1, 4-dichlorobenzoic acids, were found to be effective.

The present author has found that *p*-tolylsulfonylacetic acid, which has been prepared by Gabriel[3] from sodium *p*-toluenesulfinate and monochloroacetic acid, is also effective as a component of the polymerization-initiating system.

$$CH_3C_6H_4SO_2Na + ClCH_2COOH = CH_3C_6H_4SO_2CH_2COOH + NaCl$$

In the present paper, per-cent-conversion of the bulk polymerization of methyl methacrylate initiated by the system of *p*-tolylsulfonylacetic acid and dimethylaniline is given, and the effects of *p*-substituted groups in dimethylaniline upon the polymerization-initiating efficiencies of the two systems, trichloroacetic acid-dimethylaniline and *p*-tolylsulfonylacetic acid-dimethylaniline, are compared.

The polymerization was carried out in the atmosphere of nitrogen. In Table I, per-cent-conversion of the bulk polymerization at 60°C is given. Each of *p*-tolylsulfonylacetic acid, and dimethylaniline alone was not responsible for the initiation of the polymerization. In Fig. 1, per-cent-conversion after 1 hr., in the bulk polymerization, by means of equimolar amounts of *p*-tolylsulfonylacetic acid and dimethylaniline at temperatures of 51, 60 and 70°C are plotted against the concentration of the acid. It is observed that the per-cent-conversion after 1 hr. is linearly dependent upon the concentration of the acid. This fact indicates that, in this polymerization, the linear dependence of the rate of polymerization upon the initial concentration of *p*-tolylsulfonylacetic acid or dimethylaniline holds, as in the case of the

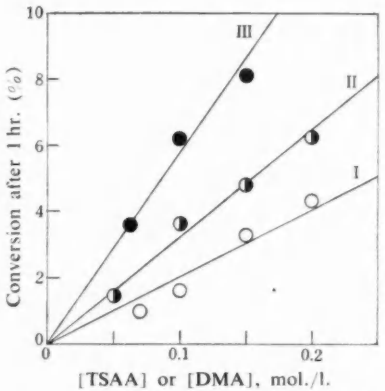

Fig. 1. Correlations of per-cent-conversion after 1 hr. with the concentration of *p*-tolyl-sulfonylacetic acid or dimethyl aniline.
I at 51°C, II at 60°C, III at 70°C

TABLE I. PER-CENT-CONVERSION (*C*) AND AVERAGE DEGREE OF POLYMERIZATION (*DP*) IN THE BULK POLYMERIZATION OF METHYL METHACRYLATE AT 60°C BY MEANS OF *p*-TOLYLSULFONYLACETIC ACID (TSAA) AND DIMETHYLANILINE (DMA)

mol./l.		Time, hr.	*C*, %	*DP*
TSAA	DMA			
0.15	0.15	1	4.8	
〃	〃	2	10.9	2120
〃	〃	3	15.3	2470
〃	〃	4	21.0	2500
〃	〃	5	27.8	
〃	〃	6	33.6	3900
〃	〃	10	97.3	
0.36	0	1	0	
〃	0	8	trace	
0	0.18	1	0	
0	0.30	10	0	

1) J. Lal et al., *J. Polymer Sci.*, **24**, 81 (1957).
2) R. Uehara, This Bulletin., **31**, 685 (1958).
3) S. Gabriel, *Ber.*, **14**, 834 (1881).

polymerization initiated by equimolar amounts of trichloroacetic acid and dimethylaniline[2], because per-cent-conversion after 1 hr., can be considered to be proportional to the initial rate of polymerization.

p-Substituted groups in dimethylaniline significantly affect the polymerization-initiating efficiencies of the two systems, *p*-tolylsulfonylacetic acid-dimethylaniline and trichloroacetic acid-dimethylaniline. Table II shows per-cent-conversions after 1 hr. by using various dimethylanilines in bulk polymerizations of methyl methacrylate, in which *p*-tolylsulfonylacetic and trichloroacetic acids were used respectively. Electron-donating groups such as methyl and methoxyl promote, and electron-withdrawing groups such as chloro, bromo and nitroso reduce the efficiencies of the polymerization-initiating systems. In Table II, C/C_0 are also shown, where C_0 and C are per-cent-conversions in the polymerizations by using dimethylaniline and *p*-substituted dimethylaniline, respectively.

TABLE II. RELATIVE EFFICIENCY OF *p*-SUBSTITUTED DIMETHYLANILINE IN THE POLYMERIZATIONS INITIATED RESPECTIVELY BY SYSTEMS, *p*-TOLYLSULFONYLACETIC ACID-DIMETHYLANILINE AND TRICHLOROACETIC ACID-DIMETHYLANILINE

Substituent	% Conversion* (TSAA and DMA)	C/C_0	% Conversion** (TCA and DMA)	C/C_0
OCH_3	11.3	2.35	11.4	1.752
CH_3	8.7	1.81	8.9	1.37
H	4.8	1.0	6.5	1.0
Cl	2.9	0.604	4.2	0.646
Br	2.4	0.500	4.1	0.630
NO	0	0	0	0

* 0.15 mol./l. of each of TSAA and DMA were used at 60°C.

** 0.20 mol./l. of each of TCA and DMA were used at 25°C.

For each of the substituted groups, the value of C/C_0 in the polymerization by using *p*-tolylsulfonylacetic acid is substantially similar to that in the polymerization, in which trichloroacetic acid was employed, i.e., the relative efficiency of *p*-substituted dimethylaniline is substantially the same in the initiating systems. When the logarithms of C/C_0 are plotted against σ (substitutent constant of Hammett) of each substituted groups, good straight lines are obtained as are shown in Fig. 2. It is evident that Hammett's rule holds in the two cases.

As has been mentioned above, the dependence of the initial rate of polymerization upon the concentration of *p*-tolylsulfonylacetic acid (or dimethylaniline) and the relative efficiency of the substituted dimethylaniline in the polymerization of methyl methacrylate initiated by the system of *p*-tolylsulfonylacetic acid and dimethylaniline are quite similar to those in the polymerization initiated by a combined action of trichloroacetic acid and dimethylaniline. Therefore, it is conceivable, that the polymerization initiated by *p*-tolylsulfonylacetic acid and dimethylaniline proceeds through the same mechanism as that which has been postulated previously for the polymerization initiated by trichloroacetic acid and dimethylaniline[2].

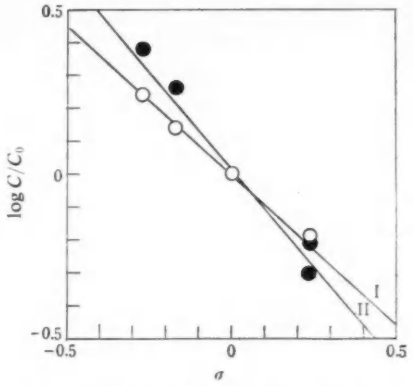

Fig. 2. Correlations of $\log C/C_0$ with σ.
I for TCA and DMA (○)
II for TSAA and DMA (●)

Experimental

The polymerization and the purification of methyl methacrylate were carried out as mentioned previously[2]. *p*-Tolylsulfonylacetic acid was prepared by the following procedures; sodium *p*-toluenesulfinate (43 g.) and monochloroacetic acid (19 g.) were mixed with methanol (100 cc.), and sodium hydroxide (8 g.) which was dissolved in water (100 cc.) was added. The mixture was refluxed for 4 hr., and then methanol was distilled off. By treating the residue of the distillation with 30% aqueous hydrochloric acid (50 cc.), an oily material separated. The oil was cooled in an ice salt-bath until it changed into crystalline solids. They were washed with aqueous methanol (1 : 1 by volume) and recrystallized from pure methanol, giving pure *p*-tolylsulfonylacetic acid (17.5 g.), m. p. 86°C. Dimethylaniline and *p*-substituted dimethylaniline were distilled under reduced pressure in the atmosphere of nitrogen or recrystallized from methanol: dimethylaniline b. p. 56°C/5 mmHg, $-CH_3$ b. p. 73.5°C/5 mmHg, $-Cl$ b. p. 86°C/5 mmHg, $-Br$ b. p. 101°C/5 mmHg, $-OCH_3$ m. p. 48.5°C, and $-NO$ m. p. 85°C.

Summary

It has been found that the polymerization of methyl methacrylate is initiated by the system of *p*-tolylsulfonylacetic acid and dimethylaniline.

In the polymerization initiated by equimolar amounts of *p*-tolylsulfonylacetic acid and dimethylaniline, the initial rate of polymerization is linearly dependent upon the initial concentration of the acid (or dimethylaniline). Hammett's rule holds for the relative efficiency of *p*-substituted dimethylaniline as the component of the polymerization-initiating system. These relationships are quite similar to those which are observed in the polymerization of methyl methacrylate, initiated by trichloroacetic acid and dimethylaniline. It is conceivable that the two polymerization reactions proceed through the same mechanism.

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*Kolbe's Reaction of Higher Fatty Acids. I. Electrolysis of Lauric Acid**

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(Received August 21, 1959)

Kolbe's reaction of fatty acids in general has been studied by many investigators but that of lauric acid[1] in particular not in detail. In the previous paper[2], one of the present authors, R. Matsuda, studied electrolysis of acetic and propionic acids for the purpose of clarifying the mechanism of the reaction. The present study was undertaken to find a clue to approach its true aspect, dealing with higher members of fatty acid.

Four electrolytes were employed which consisted of an ethanolic solution of lauric acid and potassium hydroxide. These were different from each other with respect to the alkali content. In Experiment 1 the effect of changing anodic current density 0.08~1.20 amp./cm^2 upon the current efficiency of docosane production which is due to Kolbe's reaction was examined with one of the electrolytes. The increase of current efficiency with that of the anodic current density was observed with nickel anode as well as platinum anode. The former anode resulted in current efficiency which was close, but a little inferior, to that by means of the latter.

In Experiment 2 the effect of the alkalinity of the electrolyte upon the current efficiency was examined with the four solutions, and it was found that the less alkaline the electrolyte, the greater was the current efficiency. Nickel and platinum anodes behaved as in Experiment 1. In the case of lower members of fatty acid, nickel anode is known not to give rise to Kolbe's reaction.

Experimental

An anode of platinum plate was coupled with a cathode of the same material, and so was an anode of nickel plate with a cathode of the same. The cathode in each case was in the shape of a square box without top or bottom, the horizontal section being 10×20 mm., and the height 20 mm. The anode which was rectangular 5×10 mm. was placed at the center of the cathode in each case. The upper part of the electrlytic cell was cylindrical 100 mm. long and 30 mm. in diameter, and its lower part was 50 mm. long, being flattened so as to have the two faces 25 mm. apart. The vessel was inclined by some 30° when in operation. Such a cell together with the electrodes helped not only to lessen the volume of the electrolyte and the voltage required, but also to ease the agitation of the solution without mechanical device. This sort of agitation might have the disadvantage of not always being uniform, because of the varied amount of evolving gas. It was, however, sufficiently useful for the present purpose. The lauric was 99.9% pure, the neutralization value being 279.5 against the theoretical value of 280.23 and the m. p. 44.1°C. Four solutions were prepared for electrolysis, each of which contained 1 mol. lauric acid and a different portion of potassium hydroxide in a mixture of 800 cc. ethanol and 533 cc. water: Solutions A, B, C and D contained 0.14, 0.34, 0.68 and 1.02 mol. potassium hydroxide respectively.

Each electrolysis was conducted with 40 cc. of the solution at 40°C. An oily mass floated, consisting mainly of docosane, as it was produced by

* Read before the Local Meeting of the Chemical Society of Japan at Tokushima, August 29, 19588.

** Present address, Daitoh Paper Mill Co., Iyo-Mishima, Ehime.

1) J. Petersen, *Z. Electochem.*, **12**, 143 (1906); Y. Minami, F. Ono and Y. Toyama, *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*), **53**, 393 (1950).

2) R. Matsuda, This Bulletin, **7**, 18, 297 (1932).

electrolysis. The content of the vessel was cooled after electrolysis, and the coagulated crude docosane was taken out, melted in 70~80°C water, and cooled again. This product was purified by extracting with benzene four to five times, and then by recrystallizing with ethanol three to four times. It was subsequently identified as docosane by the melting point, the elementary analysis and the molecular weight determination. M. p. 44.0~44.5°C (the reported m. p. 44.4°C)[3].

Found: C, 85.30; H, 14.81. Calcd. for $C_{22}H_{46}$: C, 85.39; H, 14.61%. Mol. wt. (Rast's method). Found: 292. Calcd.: 310.31.

Experiment 1. Solution C was electrolyzed with the nickel as well as the platinum electrodes. The anodic current density was varied 0.08~1.20 amp./cm² in order to see the influence of anodic current density on Kolbe's reaction, 2200 coulombs were supplied for each electrolysis. This quantity was nearly 90% of that necessary to electrolyze lauric acid in the solution. The docosane production is shown in Table I and Fig. 1.

Table I. Influence of anodic current density upon docosane production

Anodic current density amp./cm²	Pt-electrodes docosane current efficiency		Ni-electrodes docosane current efficiency	
	g.	%	g.	%
0.08	1.20	34.0	1.12	31.8
0.20	1.23	34.8	1.21	34.3
0.40	1.31	37.1	1.27	36.0
0.80	1.39	39.4	1.30	36.8
1.20	1.42	40.2	1.35	38.2

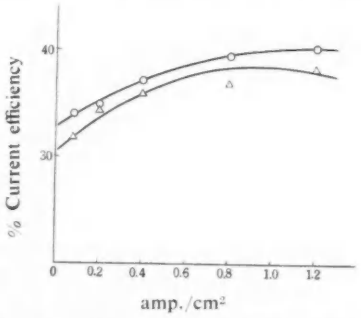

Fig. 1. Influence of anodic current density upon docosane production.
-○- Platinum electrodes.
-△- Nickel electrodes.

Experiment 2. In order to see the influence of alkalinity, solutions A, B, C and D were electrolyzed with 2200 coulombs at a constant anodic current density of 0.4 amp./cm², employing the platinum as well as the nickel electrodes. The current efficiency of docosane production in these cases is shown in Table II and Fig. 2.

Table II. Influence of alkalinity of solution upon docosane production

Solution	Mol. KOH per 1 mol. lauric acid	Pt-electrodes Docosane	C. E.	Ni-electrodes Docosane	C. E.
A	0.14	2.29g.	64.9%	2.23g.	63.2%
B	0.34	1.88	53.3	1.88	53.3
C	0.68	1.31	37.1	1.27	36.0
D	1.02	0.67	19.0	0.54	15.3

C. E. denotes current efficiency.

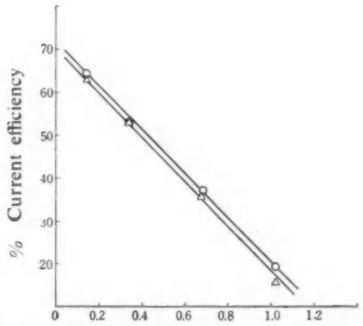

Fig. 2. Influence of alkalinity of solution upon docosane production.
-○- Platinum electrodes.
-△- Nickel electrodes.

Discussion

According to Experiment I the increase of anodic current density favored Kolbe's reaction, the influence being more noticeable when the current density was smaller. This tendency was also observed with acetic acid, in which case it was mentioned that proper regions of concentration and pH should be maintained[4]. Larger current density means a larger number of anions discharged per unit surface area of the anode. The result of Ex-periment I will be understood if it is assumed that the discharge of lauric acid anions which is responsible for Kolbe's reaction occurs dominantly under the favored condition. When the current density was larger than 1.2 amp./cm², the gas evolution made it impossible to keep the current uniform and to obtain a reliable result. It is presumed that docosane production decreases for the following two reasons: first that with current density above 1.2 amp./cm² the discharge of more easily movable hydroxyl ions might dominate, and second that the migration velocity of lauric acid ions reaches the maximum. Docosane production consequently decreased.

3) The reported value: 44.0~44.5°C, F. Kraft, *Ber.*, **40**, 4783 (1907).

4) R. Matsuda, *J. Chem. Soc. Japan (Nippon Kwagaku Kwaishi)*, **51**, 662 (1930).

Platinum and nickel were compared as anode material. The latter was found as good for Kolbe's reaction of lauric acid as the former, which had been regarded practically as the superlative material for Kolbe's reaction of fatty acid in general.

It was shown by Experiment 2 that docosane production quickly dropped off with the increase of potassium hydroxide, and there was no maximum point in the curves of Fig. 2 as was expected. It seems that the discharge of lauric acid ions steadily gave place to that of hydroxyl ions as potassium hydroxide increased, and docosane production decreased. Platinum and nickel were compared again as anode material and found close to each other with respect to the current efficiency of docosane production, although the former was superior to the latter as in Experiment 1. Fichter[5] considered that oxidation of fatty acid by means of anodic atomic oxygen resulted in Kolbe's reaction. There is, however, a great difference between the oxygen overvoltages of platinum and nickel. If the overvoltage should have anything to do with anodic atomic oxygen, hence with Kolbe's reaction, these two metals would behave differently as anode material, platinum with its high over-voltage being favorable to the reaction. Besides, Kameyama[6] describes that when acetate is electrolyzed with nickel, iron or gold as an anode no Kolbe's reaction takes place, oxygen being the dominant product of the anodic reaction.

In addition to the fact that nickel was available as an good anode for Kolbe's reaction in the present case, dimethlyglyoxime failed to detect nickel ions in the electrolyzed solution, and the nickel anode showed no apparent change after electrolysis. It is likely that the nickel anode assumed the passive state during electrolysis.

The authors wish to express their thanks to Nippon Oils and Fats Co., Ltd. which kindly provided them with lauric acid.

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5) Fr. Fichter, *Trans. Am. Electrochem. Soc.*, **45**, 131 (1924).

6) N. Kameyama, "Theory and Application of Electrochemistry (Denki-Kagaku no Riron oyobi Oyo)" Vol. II. Maruzen, Tokyo (1953), p. 225.

Coprecipitation of Neptunium with Lanthanum Trifluoride

By Eiko NAKAMURA

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It is well known that oxidized neptunium does not coprecipitate with lanthanum trifluoride whereas reduced neptunium is carried down almost quantitatively. Although this process is studied and often utilized for the practical separation of neptunium[1-3], its oxidation state is not clearly defined. Some believe that both neptunium(IV) and -(V) are carried down by lanthanum trifluoride[4], whereas others believe that neptunium(V) is not[5]. Sometimes the expression the "lanthanum fluoride carriable state" is used in place of the "oxidation state"[6]. Thus, the coprecipitation behavior of neptunium (V) is open to question.

In the present study, the different modes of coprecipitation behavior of neptunium(IV), -(V) and -(VI), are studied with the aids of the tracers for neptunium(IV), -(V) and -(VI). The oxidation state of the neptunium tracer used is determined according to the solvent extraction behavior as well as to the coprecipitation behavior with zirconium phosphate.

Experimental

Materials.—Neptunium-239 separated from neutron irradiated uranyl nitrate[7] is used as the tracer for neptunium. Prior to use, the tracer is treated chemically in order to confirm the fact that neptunium(IV), -(V) and -(VI) tracer is radiochemically pure.

1) G. T. Seaborg and A. C. Wahl, *J. Am. Chem. Soc.*, **70**, 1128 (1948).
2) L. B. Magnusson and T. J. LaChapelle, ibid., **70**, 3534 (1948).
3) L. B. Magnusson, S. G. Thompson and G. T. Seaborg, *Phys. Rev.*, **78**, 363 (1950).
4) L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, AEC Report ANL-4066 (1947).
5) G. T. Seaborg and J. J. Katz, "The Chemistry of the Actinide Elements"; Methuen and Co., Ltd., London (1957), Chap. VI.
6) E. K. Hyde, First United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. VII, P/728, United Nations Publication, New York (1956).
7) T. Ishimori and E. Nakamura, This Bulletin, **32**, 713 (1959).

These chemical treatments are as follows.

Tetravalent neptunium.—(A) *In nitirc acid system.* The tracer reduced by granulated zinc in 1 N nitric acid is extracted by TTA*-benzene, stripped by 3 N nitric acid washed with benzene and diluted with distilled water to 2 N. (B) *In hydrochloric acid system.* The tracer is reduced by granulated zinc in 1 N HCl, extracted by TTA-benzene solution, stripped by 1 N HCl in a large volume and washed with benzene.

Pentavalent neptunium.—In the nitric acid system, neptunium(V) tracer is prepared in the following four ways. (C) The tracer is prepared as perchloric acid solution and pipetted into 2 N nitric acid. Neptunium is almost all pentavalent in perchloric acid[7], and the neptunium(VI) which might be present is removed by 100% TBP**. (D) The tracer is oxidized with ceric ammoium nitrate[5] in 7 N nitric acid, extracted with 100% TBP, stripped by distilled water after the organic layer is diluted with a large volume of benzene, and reduced by hydrazine[5]. The acid concentration is about 2 N. Neptunium distribution ratios in the TBP nitric acid system are measured when neptunium is treated with oxidizing or reducing agent. (E) The tracer is reduced with sulfur dioxide in perchloric acid solution in order to change all of neptunium into neptunium(V), and pipetted in volume of a few lambda (0.001ml.). The distribution ratio is measured between 100% TBP and 1.7 N perchloric acid tracer solution saturated with sulfur dioxide. (F) The tracer is treated as (D), but reduced with sulfur dioxide instead of with hydrazine[5]. The distribution ratio of this tracer solution is checked between 1.7 N perchloric acid and TBP.

(G, H) In the hydrochloric acid system, the tracer is obtained in perchloric acid solution and a few lambda of it are pipetted into the acid. The acid concentration is 1 N(G) or 4 N(H) of hydrochloric acid.

(I, J) In the perchloric acid system, a perchloric acid tracer solution is used. The perchloric acid concentration is 4.6 N(I) or 1.2 N(J).

Hexavalent neptunium.—(K) In nitric acid system. The tracer solution is warmed and oxidized with ceric ammonium netrate in 7 N HNO_3[5]. Oxidized neptunium is extracted with 100% TBP. The organic phase obtained is shaken with 7 N nitric acid in order to remove Np(IV) and -(V). Neptunium is backextracted with distilled water and washed with benzene. The acid concentration is about 2 N. The distribution ratio of neptunium between 7 N nitric acid and TBP is measured. (L) In hydrochloric acid system. The tracer is oxidized by potassium chlorate[5] in 8 N hydrochloric acid during the heating of the solution, extracted with 100% TBP, backextracted with a large volume of distilled water, and washed with benzene. The distribution ratio of tracer between 8 N hdyrochloric acid and 100% TBP is checked. (M) In perchloric acid system. Tracer is oxidized with silver peroxide in 1.2 N perchloric acid[5]. Experiments are carried out in the presence of silver peroxide powder. Without silver peroxide, the tracer is carried down with lanthanum fluoride.

The lanthanum carrier solution contains 2 mg. of the lanthanum ion per ml. in acid solution. In order to avoid complexities, lanthanum carrier is dissolved in the same acid as that used for nuptunium tracer solution in every case.

The zirconium carrier solution contains 10 mg. zirconium per ml.

Hydrofluoric acid (47.1%) is used without dilution as precipitant for lanthanum fluoride. It will be seen in Table I that high hydrofluoric acid concentration in the precipitant causes marked coprecipitation of neptunium(V) in nitric acid medium. Thus, the coprecipitation behavior is supposed to be dependent on the concentration of hydrofluoric acid. However, not considering this effect, hydrofluoric acid is used without any dilution or purification in the present study.

1 M diammonium hydrogen phosphate solution is used as precipitant for zirconium phosphate.

Procedure.—The coprecipitation experiments are carried out as follows. Two milliliters of acid solution containing neptunium-239 in a desired oxidation state, 1 ml. of carrier solution and 1 ml. of precipitant solution are mixed thoroughly in a centrifuge tube. The hydrofluoric acid corrosion of glass is avoided by using an polyacrylic acid tube. After the white precipitate is removed by centrifugation, 2 ml. of the supernatant solution is taken in a glass tube for the measurement of the gamma activity. This is measured by Philips' scintillation counter.

Results

The reproducibility is checked by repeating experiments under the same conditions. As is seen in Table I, most values coincide well with

Table I. The effect of hydrofluoric acid concentration

Acid concn.	Activity remaining / Activity taken	Mean
conc. HF(47.1%)	0.0067	0.0073
	0.0068	
	0.0082	
	0.0074	
1 : 1 HF	0.010	0.010
	0.011	
	0.0096	
	0.0096	
1 : 3 HF	0.057	0.057
	0.044	
	0.060	
	0.060	

Given activity for 2 ml. of solution is 61486 cpm. Nitric acid concentration is 2 N. Tracer is Np(V).

Table II. The effect of nitric and concentration

HNO_3, N	Activity remaining / Activity taken
0.5	0.0138
1.0	0.0116
2.0	0.0124
5.0	0.0110

* Thenoyltrifluoroacetone.
** Tri-*n*-butyl phosphate.

TABLE III. COPRECIPITATION OF NEPTUNIUM

Acid	Tracer		LaF_3 pptn.		$ZrH_2(PO_4)_2$ pptn.	
	Solution	Treatment	Ratio*	% Np pptd.	Ratio*	% Np pptd.
HNO_3	Np(IV)	A	0.0096	99	0.084	92
	Np(V)	B	0.012	99	0.70	30
	Np(V)	C	0.0064	99	0.77	23
	Np(V)	D	0.017	98	0.78	22
	Np(V)	E	0.021	98	0.85	15
	Np(VI)	F	0.99	1	0.45	55
HCl	Np(IV)	G	0.016	98	0.018	98
	Np(V)	H	0.011	99	0.96	4
	Np(V)	I	0.0099	99	0.87	13
	Np(VI)	J	0.72	28	0.75	25
$HClO_4$	Np(V)	K	0.028	97	0.97	3
	Np(V)	L	0.026	97	0.82	18
	Np(VI)	M	0.89	11	0.66	34

* $\frac{\text{Activity remaining in solution}}{\text{Activity taken}}$

one another. However, experiments are repeated four times under the same conditions and the mean value of the ratio between the neptunium remaining and the neptunium taken, is calculated.

On the other hand, it is likely that the acidity of the tracer solution would not cause a strong effect on the coprecipitation. Table II shows that the tracer solution of 0.5～5.0 N nitric acid gives reproducible results. All results obtained are summarized in Table III.

The tracers were prepared by solvent extraction with TBP and/or TTA, as described in the experimental part and the oxidation state of the neptunium was determined according to the solvent extraction behavior and also the coprecipitation behavior with zirconium phosphate.

The oxidation state of neptunium(IV) was ascertained by TTA-extraction and zirconium phosphate coprecipitation. It is well known that only neptunium(IV) is extracted by TTA[4-9], and is carried down by zirconium phosphate[3,5,6]. Results show that neptunium(IV) coprecipitates with lanthanum fluoride in nitric and hydrochloric acid solutions. No experiment was carried out in perchloric acid solution, because neptunium(IV) is unstable in perchloric acid solution.

In the series of experiments for neptunium(V) and -(VI), the distribution ratios of the neptuium tracer were measured between mineral acid and 100% TBP. The distribution of neptunium(IV), -(V) and -(VI) between tributyl phosphate and some kinds of mineral acid had been betermined in the previous study[7]. The distribution ratio being measured, the oxidation state is assigned by comparing the distribution ratio measured and that reported. On the other hand, zirconium phosphate can not carry down neptunium(V) and -(VI) quantitatively. These results show that neptunium(V) is carried down with lanthanum fluoride whereas neptunium(VI) is not. An uncertainty may be found in the preparation of $ZrH_2(PO_4)_2$ precipitate, because it is not aged in order to prevent any change in the oxidation state of neptunium.

It will be noted in Table III that both neptunium(IV) and -(V) are carried down by lanthanum fluoride almost completely, while a remarkable amount of neptunium(VI) remains in the supernatant solution. As far as lanthanum fluoride precipitation is concerned, the difference between the behavior of neptunium(IV) and that of neptunium(V) can not be identified separately, but these two oxidation states behave quite differently in TBP-acid solution systems. It is also seen in Table III that they behave differently in coprecipitation with zirconium phosphate.

Results show that neptunium(IV) and -(V) can not be separately identified according to their behavior in being carried down with lanthanum trifluoride, whereas they are identified by the behavior in the solvent extractions or in the coprecipitation with zirconium phosphate. Thus it is presumed that both neptunium(IV) and -(V) are carried down almost completely with lanthanum trifluoride while neptunium(VI) remains in the supernatant solution.

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On the Molecular Structure of Malononitrile

By Eizi HIROTA and Yonezo MORINO

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The structure of malononitrile molecule has been investigated by microwave spectroscopy[1], three kinds of isotopic species, $CHD(CN)_2$, $CD_2(CN)_2$, and $CH_2CNC^{15}N$, being used in addition to the normal one, $CH_2(CN)_2$. The CCN group was found to be bent slightly. However, as Dr. N. Muller pointed out in his private communication, the procedure of the analysis applied gave a mixed r_s and r_o structure, that is, the positions of hydrogen and nitrogen atoms were determined by isotopic substitution, on the other hand those of carbon atoms were obtained from the first moment equation and the observed moments of inertia, because the isotopic atom ^{13}C was not available[2]. It would be therefore worthwhile to see whether the bent structure of the CCN group is established or not, in the r_o structure including inertia defect. The reanalysis is made by fitting the calculated x-, y-, and z-moments with the observed by the least-squares method. The result is shown in Table I and the molecular structure obtained is listed in Table II. It is found within the mean deviation that the CCN group is bent by $3°40' \pm 2°54'$[3]. The bond lengths C–C and C≡N are nearer to those found in a number of other related molecules than those obtained in the previous paper, though the mean deviations attached are large enough to include the structural parameters determined by the previous analysis.

It is very difficult to estimate the errors in the molecular structure obtained. The effect of zero-point vibration is a serious factor in the determination of molecular structure by the spectroscopic method. The mean deviations given here are considered mostly due to the effect of zero-point vibration. The error in the observed moment of inertia is of minor importance, and was taken into consideration in the previous paper where the effect of zero-point vibration was ignored. The more detailed analysis will be made possible by using the ^{13}C species.

TABLE I. THE x-, y-, AND z-MOMENTS (amu Å^2)

	$CH_2(CN)_2$		$CH_2CNC^{15}N$		$CD_2(CN)_2$		$CHD(CN)_2$	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
$\sum m_i x_i^2$	1.4124	1.4102	1.4106	1.4102	2.9872	2.9847	2.1805	2.1856
$\sum m_i y_i^2$	170.3922	170.3574	175.1228	175.1228	170.3236	170.3574	170.3564	170.3574
$\sum m_i z_i^2$	22.7964	22.7991	23.0876	23.0877	27.4036	27.4065	25.1430	25.1374

TABLE II. MOLECULAR STRUCTURE OF MALONONITRILE

	r_o structure	r_o and r_s structure[a]
C–C	1.468 ± 0.034 Å	$1.480_8 \pm 0.0056$ Å
C≡N	1.167 ± 0.026 Å	$1.146_6 \pm 0.0064$ Å
C–H	1.088 ± 0.010 Å	$1.090_6 \pm 0.0034$ Å
∠CCC	$109°22' \pm 2°54'$	$110°24 \pm 24'$
∠HCH	$108°42' \pm 1°22'$	$108°26' \pm 26'$
∠CCN	$180° - (3°40' \pm 2°54')$ (outside)	$180° - (3°24' \pm 26')$ (outside)
Δ	0.333 ± 0.015 amu Å^2	0.3379 amu Å^2

a) See Ref. 1.

1) E. Hirota and Y. Morino, This Bulletin, **33**, 158 (1960).
2) C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958).
3) C. C. Costain and J. R. Morton, (ibid., **31**, 389 (1959)) have shown that the C–C≡C group in propynal is bent by 1°36′.

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The Equilibrium between the Sn-Pb Liquid Solution and the H_2-H_2O Gaseous Mixture

By Koji ATARASHIYA*, Masahiro UTA**, Mitsuo SHIMOJI and Kichizo NIWA

(Received September 28, 1959)

The thermodynamic investigation of metallic solutions is very important in order to have a deep understanding of their structure[1]. In the tin-lead system the primary solid solutions have very limited solid solubilities in the respective solvents. The immiscibility of these primary solid solutions is found over a wide range of the concentration[2]. This fact may reflect the fact that the excess heat of the tin-lead liquid solution shows a positive value according to the simple model of solutions, for example, that of the regular solution[3]. Thermodynamic data on this binary system, all of which have been based on calorimetric measurements, enable one to confirm the above expectation. The excess heat of this system has been measured by Magnus and Mannheimer[4], by Kawakami[5], by von Samson-Himmelstjerva[6], and by Kleppa[7].

However, no direct measurement of the excess free energy of this system has so far been carried out. This may presumably be due to some experimental difficulties which accompany the direct methods of measuring the activity of this system such as those of electromotive force and of vapor pressure. The activities of the tin-lead system have been calculated by Elliott and Chipman[8] from the experimental results on the tin-lead-cadmium system.

In this paper the activity of tin in the tin-lead liquid solution is obtained by measuring the equilibrium of the tin-lead system with the hydrogen-water vapor mixture.

The principle of this method is as follows:—

If the hydrogen-water vapor mixture is in equilibrium with liquid tin and its dioxide in accordance with Eq. I,

$$Sn(l) + 2H_2O(g) = SnO_2(s) + 2H_2(g) \qquad (I)$$

one can write, as the equilibrium constant K for reaction I,

$$K = (P_{H_2}/P_{H_2O})^2 \qquad (1)$$

where P_{H_2} and P_{H_2O} are the partial pressures of H_2 and H_2O respectively. On the other hand, a similar equation (II) can be given for the tin-lead liquid solution, if the oxide of tin is stable as compared with that of lead.

$$Sn(\text{liq. soln.}) + 2H_2O(g) = SnO_2(s) + 2H_2(g) \qquad (II)$$

Corresponding to Eq. 1, one has

$$K = (P_{H_2}'/P_{H_2O}')^2/a_{Sn} \qquad (2)$$

where a_{Sn} is the activity of tin relative to pure liquid tin, and the prime labeled for the pressures means the equilibrium partial pressure in the tin-lead system. From Eqs. 1 and 2 one obtains

$$a_{Sn} = (P_{H_2}'/P_{H_2O}')^2/(P_{H_2}/P_{H_2O})^2 \qquad (3)$$

Thus, in principle, the activity of tin in this system can be determined by measuring the partial pressures of hydrogen and water vapor in equilibrium with both pure tin and tin-lead.

Stability of Oxides

It is the fundamental condition for Eq. 3 that the oxide, SnO_2, is most stable among all oxides conceivable in the present system. In thermodynamic terms, an oxide should be stable in case the partial pressure of oxygen in equilibrium with the oxide is low. In other words the formation of a stable oxide is associated with a small amount of oxygen. In Table I the partial pressures of oxygen in equilibrium with several oxides are shown, which are calculated from the free energies of formation of respective oxides[9] at 1000°K.

It is readily found that tin oxides are stable

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1) K. Niwa and M. Shimoji, *Proceedings of International Symposium on Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, Teddington, England (1958).
2) M. Hansen and K. Anderko, "Constitution of Binary Alloys", McGraw-Hill, New York (1958).
3) E. A. Guggenheim, "Mixtures", Oxford Univ. Press, London (1952).
4) A. Magnus and M. Mannheimer, *Z. physik. Chem.*, **121**, 267 (1926).
5) M. Kawakami, *Z. anorg. allgem. Chem.*, **167**, 345 (1927); *Sci. Rep. Tohoku Imp. Univ.*, **16**, 915 (1927).
6) H. O. von Samson-Himmelstjerva, *Z. Metallkunde*, **28**, 197 (1936).
7) O. J. Kleppa, *J. Phys. Chem.*, **59**, 175 (1955).
8) J. E. Elliott and J. Chipman, *J. Am. Chem. Soc.*, **73**, 2682 (1951).
9) J. P. Coughlin, *Bureau of Mines, Bull.*, No. 542 (1954).

TABLE I. PRESSURES OF OXYGEN IN EQUILIBRIUM WITH TIN- AND LEAD-OXIDES AT 1000°K

Oxides		Pressures of oxygen $\log P_{O_2}$ (atm.)
SnO_2	(s)	−19.6
SnO	(s)	−19.0
SnO	(g)	− 7.1
PbO	(s)	−12.6
Pb_3O_4	(s)	− 8.9
PbO_2	(s)	− 4.5

compared with lead oxides. Although the value of SnO(s) is close to that for SnO_2(s), the solid SnO is found unstable as compared with SnO_2 in other studies[10]. Further, according to the electron diffraction study by Shimaoka and Yamai[11], the oxide film formed on the surface of the tin-lead solution under the condition of temperatures higher than 470°C and of pressures below 1 atmosphere of air, shows complete patterns of the stannic oxide. After the present experiment has been finished, the samples should be examined by means of the X-ray or by the electron diffraction, but the amount of oxides formed by reaction II is too small to be determined in such a way. However, the fact of the stannic oxide being most stable may be assured by the other reasons already described above.

Experimental

The same apparatus, used in the measurement of equilibrium in GeO_2-H_2-Ge-H_2O system[12], is employed with a modification of the sizes of both the furnace and the reaction tube.

Metallic solutions are prepared by fusing each mixture of pure metals (Kanto Kagaku, 1st grade) in a closed vessel under vacuum; their concentrations are confirmed by chemical analysis.

The boat of high alumina filled with 3∼4 g. of the powdered sample, which has been dispersed in alumina powder, is set in the reaction tube. After the tube has been evacuated to the pressure of 10^{-5} mmHg, water vapor saturated at 18±0.01°C (15.45 mmHg), is introduced for oxidation, while hydrogen, generated by electrolysis of a potassium hydroxide solution, is introduced for reduction. The oxidation method is used for liquid metallic solutions, since there is no assurance of obtaining the required metallic solution from the reduced tin metal. The rate of gas flow is about 200 cc./min. The measurements have been carried out over the range of 700∼800°C.

The whole error in a_{Sn} may be about 3% which is due to the inaccuracies of the furnace temperature (±2°C) and of the temperature of water (±0.01°C), as well as of the reading of the cathetometer (pressure: ±0.01 mmHg), etc. As one of the other sources of error, the change of concentration in liquid solutions should be taken into account, since tin in the solution is oxidized during the reaction. However, the amount of this change estimated from the volume of the reaction system (about 850 ml.) is at most 10^{-5} mol., and small compared with the initial amount of tin in solutions (at least 10^{-3} mol.). Though the vapor pressure of lead is about 10^{-2} mmHg at 700∼800°C, the rate of vaporization is then at most 10^{-5} mol./hr. Thus, this effect may be negligible because of the short time taken for the present reaction (1∼5 hr.).

Results

Equilibrium in the Sn-H_2O-SnO_2-H_2 System: —The results for this system are shown in Table

TABLE II. EQUILIBRIUM IN Sn-H_2O-SnO_2-H_2

Temperature °C	Total pressure* mmHg	Equilibrium constant (K)	$\log K$	Method
875	18.75	0.0456	−1.341	reduction
850	19.10	0.0558	−1.258	〃
825	19.45	0.0670	−1.174	〃
802	19.70	0.0757	−1.121	oxidation
800	19.80	0.0793	−1.101	reduction
777	20.20	0.0945	−1.024	〃
750	20.75	0.1177	−0.929	〃
750	20.80	0.1199	−0.921	oxidation
700	22.30	0.1994	−0.700	〃

* The pressure of water vapor is kept constant at 15.45 mmHg.

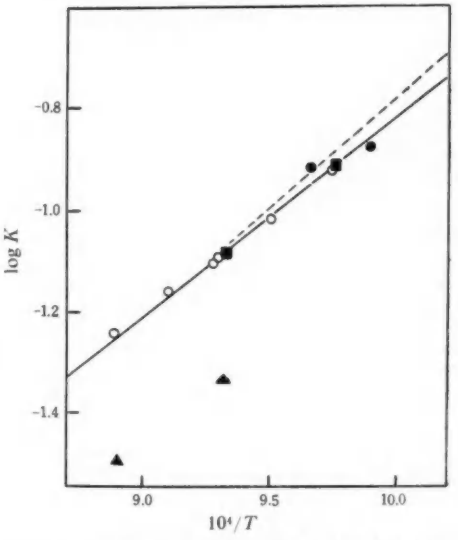

Fig. 1. Temperature dependence of equilibrium constant in the system Sn(pure)-H_2O-SnO_2-H_2
○ Present work. ● Meyer and Scheffer. ■ Emmett and Shultz. ▲ Eastman and Robinson. --- Ishikawa and Ando.

10) K. Niwa, I. Yamai and T. Wada, This Bulletin, **31**, 725 (1958).
11) G. Shimaoka and I. Yamai, *J. Chem. Soc Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **76**, 1139 (1955).
12) T. Yokokawa, M. Koizumi, M. Shimoji and K. Niwa, *J. Am. Chem. Soc.*, **79**, 3365 (1957).

TABLE III. EQUILIBRIUM IN Sn(in soln.)-H_2O-SnO_2-H_2

Temperature °C	x_{Sn}	Total pressure mmHg	$(P_{H_2}/P_{H_2O})^2$	Activity of tin	$\overline{G}^e_{Sn}$
750	0.0521	17.30	0.0143	0.116	1630
〃	0.100	17.90	0.0251	0.204	1450
〃	0.151	18.35	0.0352	0.285	1290
〃	0.199	18.70	0.0442	0.358	1190
〃	0.301	19.20	0.0589	0.477	930
〃	0.403	19.55	0.0704	0.570	700
〃	0.501	19.80	0.0793	0.642	500
〃	0.711	20.25	0.0965	0.781	190
775	0.0521	17.10	0.0114	0.115	1650
〃	0.100	17.65	0.0203	0.205	1490
〃	0.151	18.00	0.0272	0.276	1260
〃	0.199	18.35	0.0352	0.356	1210
〃	0.301	18.75	0.0456	0.462	890
〃	0.403	19.10	0.0558	0.565	700
〃	0.501	19.30	0.0621	0.628	460
〃	0.711	19.74	0.0775	0.784	200
800	0.0521	16.90	0.0088	0.110	1600
〃	0.100	17.40	0.0159	0.199	1470
〃	0.151	17.75	0.0222	0.277	1290
〃	0.199	18.00	0.0272	0.341	1140
〃	0.301	18.45	0.0377	0.472	960
〃	0.403	18.70	0.0443	0.554	690
〃	0.501	18.90	0.0499	0.624	480
〃	0.711	19.30	0.0621	0.777	180

II. If the common logarithms of the equilibrium constant, K, thus obtained, are plotted against the reciprocal temperature, as shown in Fig. 1, they lie close about a straight line, which is expressed by Eq. 4. (This equation is established by means of the least square).

$$\log K = 4150/T - 4.965 (\pm 0.05) \qquad (4)$$

This result is in good agreement with the data of other investigators[13-16]. For example, the following values are obtained by means of Eq. 4.

t, °C	K
750	0.1235
775	0.0988
800	0.0799

Equilibrium in Sn (in Soln.)—H_2O-SnO_2-H_2 System :—The equilibrium constant and the activity of tin, measured in this system, are indicated in Table III. The activity of tin, shows a positive deviation from Raoult's law, as is seen in Fig. 2. The partial excess free energy of tin, $\overline{G}^e_{Sn}$, is related to its activity by

$$\overline{G}^e_{Sn} = \boldsymbol{R}T \ln a_{Sn}/x_{Sn} = \boldsymbol{R}T \ln f_{Sn} \qquad (5)$$

where $\boldsymbol{R}$ is the gas constant, x_{Sn} is the atomic fraction of tin, and f_{Sn} is the actitvity coefficient. If the values of $\overline{G}^e_{Sn}/(1-x_{Sn})^2$ are plotted against x_{Sn}, they lie close about a straight line, shown in Fig. 3, which is expressed by Eq. 6 at 775°C.

$$\overline{G}^e_{Sn}/(1-x_{Sn})^2 = 2330 - 600(1-x_{Sn}) \quad (\pm 50 \text{ cal./mol.}) \qquad (6)$$

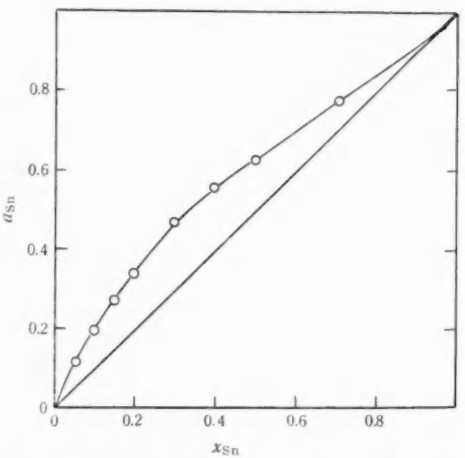

Fig. 2. Observed activity of tin in the tin-lead liquid solution at 800°C.

13) G. Meyer and F. E. C. Scheffer, *Rec. trav. chim.*, **54**, 294 (1935).
14) P. H. Emmett and J. F. Schultz, *J. Am. Chem. Soc.*, **55**, 1390 (1933).
15) E. D. Eastman and P. Robinson, ibid., **50**, 1106 (1928).
16) F. Ishikawa and S. Ando, *Sci. Paper Inst. Phys. Chem.* **34**, 873 (1938).

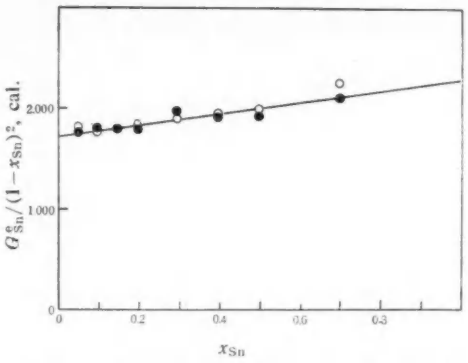

Fig. 3. Concentration dependence of partial molar excess free energy of tin in the tin-lead liquid solution. ○ Observed values at 750°C. ● Observed values at 800°C.

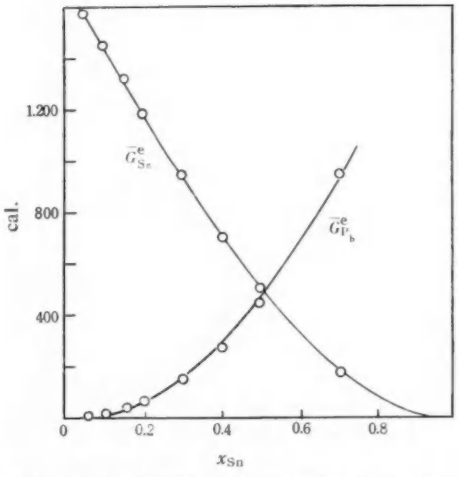

Fig. 4. Partial excess free energies in the tin-lead solution at 775°C.

Applying Gibbs-Duhem's relation to the above results, one obtains not only the partial molar excess free energy of lead, but also the (integral) excess free energy of the solutions, G^e_m, as are shown in Figs. 4 and 5 which are expressed respectively by Eqs. 7 and 8 at 775°C

$$\bar{G}^e_{Pb} = 1430\, x_{Sn}{}^2 + 600\, x_{Sn}{}^3 \qquad (7)$$

$$G^e_m = x_{Sn} x_{Pb} (1730 + 300 x_{Sn}) \qquad (8)$$

Unfortunately, the temperature dependence of a_{Sn} could not be accurately obtained in this experiment owing to the limited range of temperatures (750~800°C). This limitation is due to the fact that the vapor pressure of lead is very high at temperatures above 800°C, while the reaction rate for oxidation is very slow if the temperature is lower than 700°C.

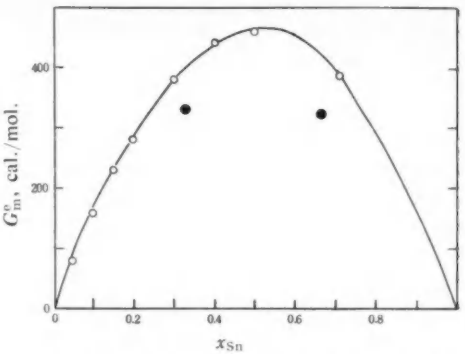

Fig. 5. Excess free energy in the tin-lead liquid solution at 775°C. ○ Observed values. ● Calculated from the data of Elliott and Chipman for the ternary system.

Discussion

So far as the excess free energy of the tin-lead system is concerned, there are no experimental data available except an indirect result calculated from those of the cadmium-tin-lead system obtained by Elliott and Chipman[8]. They have given only two values of the excess entropy at about 500°C, which can be extrapolated to 775°C. The excess free energy, G^e_m, thus obtained is as follows.

x_{Sn}	0.333	0.667
G^e_m(cal.)	333	320

By a combination of these values with the present results, a comparison is made in Fig. 5. It is found that the results, obtained by Elliott and Chipman for only two concentrations, have a tendency to represent slightly small values compared with the present ones. However, the values of the heat of mixing calculated from those for the cadmium-tin-led system are 15~20% smaller than those directly measured by Kleppa[7]. Hence, if the excess free energy is calculated by combining Kleppa's values for the excess heat with those of Elliott and Chipman for the excess entropy, the agreement between the values thus obtained and those of the present study is quite reasonable. It should be noted that the excess entropy shows a slightly negative deviation from ideal mixing.

It is of interest to examine the excess function on liquid tin-lead solutions from simplified models of metallic solutions. According to Haissinsky[17], the electronegativity of tin is almost in agreement with that of lead. (Sn^{II}, 1.65; Pb^{II}, 1.6; Sn^{IV}, 1.8; Pb^{IV}, 1.8.) So the electrochemical effect due to transfer of electrons may be very small in the tin-lead system. For

17) M. Haissinsky, *J. phys.* 7, 7 (1946).

these cases, the theoretical calculation of excess functions can be simplified, as pointed out by Hildebrand and Scott[18].

$$H_m^e = [(L_A/V_A)^{\frac{1}{2}} - (L_B/V_B)^{\frac{1}{2}}]^2 \varphi_A \varphi_B V_S \quad (9)$$

and $$S_m^e = 0 \quad (10)$$

L_A and L_B are the energies of vaporization of pure A and B respectively. V_A and V_B denote their volumes in pure states. V_S represents the volume of the solution. φ_A and φ_B are the volume fractions respectively.

As the interatomic potential in liquid metals cannot always be expressed by the well known 6-12 potentials or 6-∞ potentials, Shimoji[19] has proposed the following theoretical expression for the excess energy after taking into account the generalized potential.

$$H_m^e = [(L_A/V_A)^{\frac{1}{2}} - (L_B/V_B)^{\frac{1}{2}}]^2 \varphi_A \varphi_B V_S + \frac{nl}{8}\rho^2\left(1+\frac{\delta_v}{2}\right)\frac{L_{AA}}{V_A}\varphi_A\varphi_B V_S \quad (11)$$

Here,

$$\rho = 2(r_B - r_A)/(r_B + r_A)$$

and $$\delta_v = (L_B/V_B - L_A/V_A)/L_A/V_A) \quad (12)$$

r_i means the interatomic distance in the pure state of i. It is found that the parameter nl in Eq. 11 is about 10 or 20 in most liquid metals. If $nl = 72$, Eq. 12 corresponds to the one derived by Prigogine[20]. Of course Hildebrand's Eq. 9 can be obtained if the term due to the difference of atomic radii (size factor) is neglected in Eq. 11. Furthermore, the assumption of the geometric mean of energies between unlike atoms used in deriving Eq. 9 might be open to doubt because of metallic forces. If the arithmetic mean is used for the energies, H_m^e should be zero for Eq. 9, (or the first term of Eq. 11 should be zero.) It is noteworthy that Eq. 11 gives a positive excess energy even if the assumption of the arithmetic mean is used.

TABLE IV. COMPARISON OF CALCULATED VALUES OF THE EXCESS FUNCTIONS IN TIN-LEAD LIQUID SOLUTIONS (cal./mol.)

	Hildebrand	Shimoji ($nl=10$)	6-12 potential	Expl.
H_m^e	860(0*)	1050(200*)	2150(1300*)	330[7]
G_m^e	860	1000		460

H_m^e: The excess heat at $x_{Sn}=0.5$
G_m^e: The excess free energy at $x_{Sn}=0.5$ (at 800°C)
*: Values based upon the arithmetic mean rule.

In Table IV the calculated values of the excess energy and the exsess entropy at $x_{Sn}=0.5$ are compared with the observed ones. The most reasonable approach to the excess energy of an alloy is based on the collective electron theory of metals, such as the cellular approximation etc.[21,22] Unfortunately, no reliable values of the parameters adaptable for these theories have yet been determined either experimentally or theoretically in either the liquid tin or lead systems. However, according to Varley's calculation[21] based on the free electron approximation, the electrochemical factor is nearly zero in the lead-tin system. Then, the size factor indicating the positive excess energy plays an important role in liquid metals as well as in solid alloys. Rigorous estimation in the liquid state can not be achieved because of lack of knowledge concerning the parameters of pure metals, but the same conclusion may thus be obtained either from the theories of the pair bond interaction[18,19] or from those of the free electron approximation based upon the band model of metals.

Summary

Equilibrium in Sn (in liquid alloy)-H_2O-SnO_2-H_2 system has been determined from 750 to 800°C by measuring the ratio of pressures between H_2O and H_2 gas mixtures. From this the activity of tin liquid tin-lead solutions has been calculated, and the following equation has been derived at 775°C.

$$\overline{G}_{Sn}^e = 2330(1-x_{Sn})^2 - 600(1-x_{Sn})^3 \text{ cal. mol.}$$

The temperature dependence of $\overline{G}_{Sn}^e$ could not be determined. However, if this value is calculated by combining Kleppa's value for the excess heat, calorimetrically determined, with that of Elliott and Chipman for the excess entropy, the agreement between the value thus obtained and that of the present investigation is quite reasoable, taking into consideration the accuracies of these experiments. Theoretical considerations have been given for the excess functions of this system. It shonld be emphasized that the electrochemical effect of charge transfer is very small or may be regarded as zero in the lead-tin system and that the size factor is important.

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18) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolyte", Reinhold, New York (1950).
19) M. Shimoji, *Proceedings of International Symposium on Physical Chemistry of Metallic Solutions and Intermetallic Compounds*, N. P. L. Teddington, England (1958).
20) I. Prigogine, "Molecular Theory of Solutions", Noth Holland Publishing, (1957).
21) J. H. O. Varley. *Phil. Mag.*, **48**, 445 (1954).
22) M. Shimoji, *J. Phys. Soc. Japan*, **14**, 1525 (1959).

SHORT COMMUNICATIONS

Three Geometrical Isomers of p-Distyrylbenzene

By Soichi MISUMI and Motoyuki KUWANA

(Received February 24, 1960)

Three geometrical isomers are possible in *p*-distyrylbenzene (I) with regard to the ethylenic double bonds of the molecule. We have studied the synthesis and the photoisomerization of these three isomers with the purpose to compare the physical and chemical properties with those of the recently extensively studied pure polyolefinic systems such as diphenylpolyenes[1] and carotenoids[2].

The *cis*, *cis*- and *cis*, *trans*-isomers (I_c and I_a) were prepared by the partial hydrogenation of the corresponding acetylenic compounds using Lindlar's catalyst. The *trans*, *trans*-isomer (I_b) was obtained by the dehydration of *p*-bis(β-phenyl-α-hydroxyethyl)benzene. The isomers were purified by repeated recrystallization or chromatography on alumina.

Unexpectedly the sequence of qualitative photostability of these isomers under diffused light was found to be *trans*, *cis* (I_b) ≪ *cis*, *cis* (I_c) ≦ *trans*, *trans* (I_a). Both of the sterically hindered *cis*, *cis*- and *cis*, *trans*-isomers (I_c and I_b) showed no fine structure in their ultraviolet spectra as illustrated in Fig. 1. The *cis*, *trans*-isomer (I_b) showed the most intense

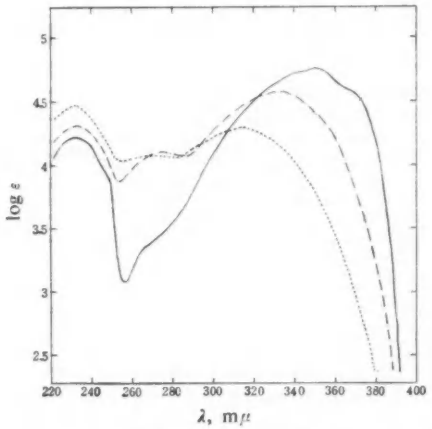

Fig. 1. Ultraviolet absorption spectra of *p*-distyrylbenzene (I) in *n*-hexane: ——, *trans*, *trans*; —·—, *cis*, *trans*; ----, *cis*, *cis*.

cis-peak[2b] (ca. 270mμ) in accord with the theory proposed by Zechmeister.

The solutions of the isomers were exposed to light of a fluorescent tube under controlled conditions and the course of the photoisomerization was followed by the change of the intensities of absorption at 270 and 350 mμ. The results are illustrated in Figs. 2 and 3. It is to be noted that the rate of spatial rearrangement of the most hindered *cis*, *cis*-isomer (I_c) is much slower than that of *cis*, *trans*-isomer (I_b). Theoretically, the same equilibrium mixture

TABLE I. PHYSICAL PROPERTIES OF *p*-DISTYRYLBENZENE

Isomer	*trans*, *trans*[3]	*trans*, *cis*[4]	*cis*, *cis*
m. p. (°C)	266~267	114~114.5	86.5~87.5
U. V. λ_{max} (mμ)	232, 350	232, 273, 331	232, 270, 314
(log ε)	(4.21), (4.76)	(4.09), (4.30), (4.56)	(4.44), (4.04), (4.22)
I. R. (cm^{-1}) *cis* δ_{CH}	—	774	774
trans δ_{CH}	966	961	—
Found* C,	93.59	93.58	93.79
H,	6.76	6.44	6.60

* Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43%.

1) L. Zechmeister et al., *J. Am. Chem. Soc.*, **64**, 2755 (1942); **69**, 553 (1947); **70**, 1937 (1948); **76**, 2308, 4144 (1954); B. C. L. Weedon et al., *J. Chem. Soc.*, **1959**, 933.

2) a) L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); *Experientia*, **10**, 1 (1954).
b) L. Zechmeister, A. L. LeRosen, W. A. Schroeder, A. Polgar and L. Pauling, *J. Am. Chem. Soc.*, **65**, 1940 (1943).

3) H. Kaufmann, *Ber.*, **50**, 515 (1917); G. Drefahl and G. Plötner, *Chem. Ber.*, **91**, 1274 (1958); T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1246 (1959).

4) J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957). He suggested that a compound melting at ca. 95°C, isolated from the products of photoisomerization of the *trans*, *trans*-isomer, may have the *cis*, *trans*-configuration.

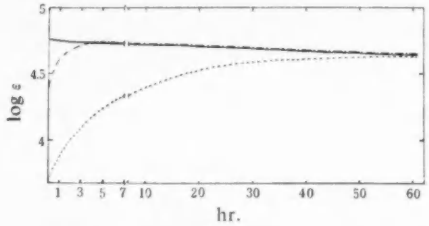

Fig. 2. Change of the extinction value at 350 mμ. of the U. V. spectra of three isomeric *p*-distyrylbenzenes in *n*-hexane by exposure to light: ——, *trans, trans*; —·—, *cis, trans*; ----, *cis, cis*.

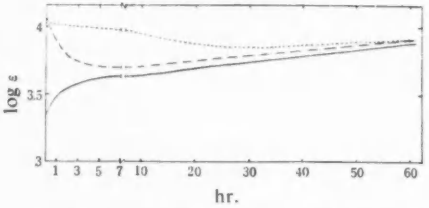

Fig. 3. Change of the extinction value at 270 mμ. of the U. V. spectra of three isomeric *p*-distyrylbenzenes in *n*-hexane by exposure to light: ——, *trans, trans*; —·—, *cis, trans*; ----, *cis, cis*.

might be attained regardless of the geometry of the starting isomers, but the experimental results showed a slight difference in their absorption spectra in final stage. This fact is attributable to the minor degree of decomposition or polymerization of I during the course of photostereomutation.

The experimental detail and the full discussion of this investigation will be published in near future.

The authors wish to express their thanks to Professor Masazumi Nakagawa for his kind advice and encouragement throughout this work.

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The Absolute Structure of Actinidine

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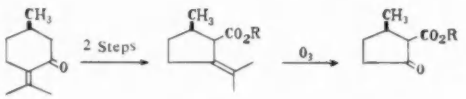
(Received March 26, 1960)

(+)-Actinidine, the enantiomeric from of the levorotatory natural product, has been synthesized from (+)-pulegone through methyl pulegenate (Ib).

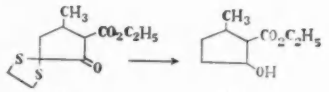
The synthesis was preceded by the scrupulous confirmation of the plane structure of pulegenic acid (Ia), presented by H. Rupe and K. Schäfer[1] to be 2-isopropyliden-5-methyl-cyclopentanecarboxylic acid. The ethyl ester (Ic) of Ia was ozonolyzed to ethyl 2-methyl-5-oxocyclopentanecarboxylate (IIc), b. p. 95~96°C/10 mmHg (Found: C, 63.31; H, 8.35. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29%), and the racemic form of the latter was synthesized.



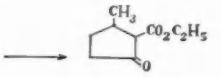
I II

a: R=H; b: R=CH_3; c: R=C_2H_5

The half ethylene dithio-ketal (III), m. p. 63°C (Found: C, 50.53: H, 6.23; S, 24.59. Calcd. for $C_{11}H_{16}O_2S_2$; C, 50.77; H, 6.20; S, 24.62%) of ethyl 2-methyl-4, 5-dioxocyclopentanecarboxylate[2] was reduced on treatment with Raney nickel to the hydroxy ester (IV) (ν_{OH} 2.89 μ in infrared absorption spectrum), which was converted into the corresponding keto ester (IIc′) by the successive oxidation with the complex of chromic oxide-pyridine. IIc and IIc′ were proved to be identical through the mixed fusion test and the comparison of the infrared absorption spectra of their semicarbazones.



III IV



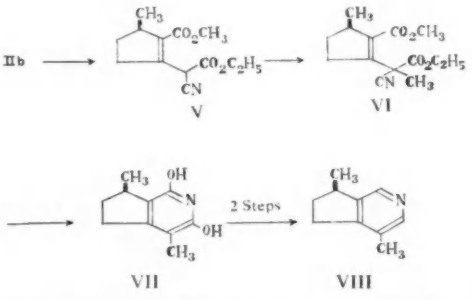
IIc′

* Institute for Food Chemistry, Kita-ku, Osaka.

1) H. Rupe and K. Schafer, *Helv. Chim. Acta*, **11**, 466 (1928).

2) H. Staudinger and L. Ruzicka, ibid., **7**, 381 (1924).

The attempts to hydroxylate the isopropyliden group in Ib with selenium dioxide under the various conditions were so all in failure that the authors were impelled to take a rather circuitous route for the purpose. The satisfactory result was achieved when the methyl ester (IIb), b. p. 90~92°C/12 mmHg (Found: C, 61.29; H, 7.91. Calcd. for $C_8H_{12}O_3$: 61.52; H, 7.75%), was chosen as a key compound and the necessary C_3-moiety was re-introduced into IIb as shown below.



The condensation product (V) of IIb with ethyl cyanoacetate was treated with methyl iodide in the ethoxide solution and the methylated diester (VI) was hydrolyzed with acid or alkali to the dihydroxypyridine derivative (VII), m. p. 172~173°C (Found: C, 67.15; H, 7.51; N, 7.98. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31; N, 7.82%). The chlorination of VII and the successive catalytic hydrogenation of the dichloro-compound, similar to those reported in the synthesis of DL-actinidine[3], yielded the base (VIII), the purified picrate (Found: C, 50.95; H, 4.36; N, 14.91. Calcd. for $C_{16}H_{16}O_7N_4$: C, 51.06; H, 4.29; N, 14.89%) of which melted at 146~147°C. The regenerated base, b. p. 88~90°C/5 mmHg, from the latter gave the value of $[\alpha]_D^{15}$ +16.1° (c 5.52 chloroform) and the identical infrared absortion chart with the natural alkaloid. Although the absolute values of rotatory power were not equal between these two actinidines obtained, the synthesized one was likely to be in a more purified state.

As the asymmetric center of (+)-pulegone had already been correlated in the stereochemical analysis to D-series[4], the absolute configuration of $C_{(7)}$-carbon atom in natural actinidine (6, 7-dihydro-4, 7-dimethyl-5(*H*)-2-pyrindine) has now been established.

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3) T. Sakan, A. Fujino, F. Murai, A. Suzui and Y. Butsugan, This Bulletin, **32**, 1155 (1959).
4) K. Freudenberg and W. Hohmann, *Ann.*, **584**, 54 (1953).

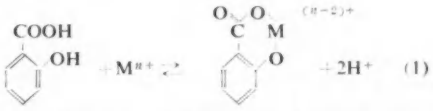
Effect of Metal Ions on the Radiation-Induced Decarboxylation of Aqueous Benzoic and Salicylic Acid Solutions

By Akira SUGIMORI and Gen-ichi TSUCHIHASHI

(Received March 9, 1960)

Remarkable effect of heavy metal ions was observed in the radiolysis of benzene in aqueous solution[1] and other organic compounds[2]. In the systems hitherto studied, the interaction between metal ions and organic molecules is expected to be different from that in the compounds containing metal ions. The effect of metal ions bound to organic molecules on the radiolysis has not yet been studied.

The present authors studied the effects of added ions on the decarboxylation of benzoic and salicylic acids, in order to clarify the difference in the effect between bound and non-bound metal ions. Benzoic acid does not form any chelate compounds with metal ions, whereas salicylic acid gives stable complexes with Fe^{3+}, Cu^{2+} and Al^{3+}.



(1)

The difference in the effect of heavy metal ions on $G(CO_2)$ was found between benzoic and salicylic acid, and this can be attributed to the difference in the states of ions.

The oxygen free solution containing 0.2% of either acid and metal salts were irradiated by ^{60}Co γ-rays in the test tube with side cell in which 0.1 N barium hydroxide solution was

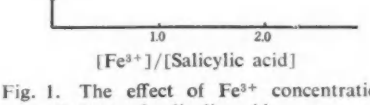


Fig. 1. The effect of Fe^{3+} concentration on $G(CO_2)$ of salicylic acid.

1) J. H. Baxendale and D. Smithies., *J. Chem. Phys.*, **23**, 604 (1955); *J. Chem. Soc.*, **1959**, 779.
2) E. A. Cherniak, E. Collinson, F. S. Dainton and G. M. Meaburn, *Proc. Chem. Soc.*, **1958**, 54.

TABLE I. EFFECTS OF SALTS ADDED ON $G(CO_2)$

Acid	Salt added	$G(CO_2)$
Salicylic acid	—	0.29
	$FeCl_3$ 1.4 mol.	1.38
	$FeSO_4$ 1.4 mol.	0.27
	$CuCl_2$ 1.4 mol.	0.47
	$AlCl_3$ 1.4 mol.	0.26
	$CoCl_2$ 1.4 mol.	0.23
	$NiCl_2$ 1.4 mol.	0.26
	$ZnCl_2$ 1.4 mol.	0.28
	$MgCl_2$ 1.4 mol.	0.28
	H_2SO_4 (0.8 N)	0.55
	H_2SO_4 (0.8 N) $FeCl_3$ 1.4 mol.	0.65
	KF 8.3 mol. $FeCl_3$ 1.4 mol.	0.11
Benzoic acid	—	0.66
	$FeCl_3$ 2.8 mol. pH~1	0.30

placed in order to absorb carbon dioxide formed. Dose rate and total dose were 9.5×10^4 r./hr. and 1.57×10^6 r., respectively. Carbon dioxide formed was absorbed by barium hydroxide solution and $G(CO_2)$ was measured volumetrically.

The effects of various metal ions are summarized in Table I. In the case of benzoic acid, Fe^{3+} added does not bring about the increase in $G(CO_2)$, while in the case of salicylic acid, it makes $G(CO_2)$ remarkably high. This suggests that Fe^{3+}, chelating organic molecules and attacking redicals cooperate in the decarboxylation of the complex. This is also supported by the following experiments.

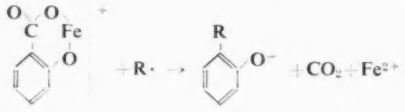
a) Fig. 1 shows the plot of $G(CO_2)$ in the radiolysis of salicylic acid against the amount of Fe^{3+} added. As is shown in the figure, a remarkable break is observed at $[Fe^{3+}]/[\text{Salicylic acid}]=1$, where all of Fe^{3+} ions and salicylic acid mulecules exist as complexes and neither of Fe^{3+} nor salicylic acid remains in excess.

b) The addition of some masking reagents such as F^- and H^+ to the complex makes $G(CO_2)$ low.

Based on the above results, the mechanism of the decarboxylation of the complexes is conceivably different from that of free acids.

Therefore the following sequence of reactions can be given for the decarboxylation of the complex.

$$H_2O \xrightarrow{\gamma\text{-rays}} H\cdot + HO\cdot + H_2O_2 \quad \text{etc.} \tag{2}$$



(3)

(where R· represents free radical)

The attacking radical (R·) is not yet identified but this mechanism is supported by the following observations.

a) In this case Fe^{3+} is easily reduced to Fe^{2+}, although it is reduced only to small extent in the absence of organic compounds.

b) Fe^{3+} and Cu^{2+} added bring about the increase in $G(CO_2)$ of salicylic acid, whereas added Al^{3+} has only a slight effect. All of them are known as metal ions which give complexes with salicylic acid.

These indicate that both the complex formation and easy reduction of metal ions are essential for this kind of metal catalyzed radiation-induced decarboxylation.

The present authors are very grateful to Dr. K. Kimura and Dr. A. Danno for their helpful discussion.

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